Winter 1967

THE STABILITY CONSTANTS OF INDIUM(III) COMPLEXES WITH CHLOROACETATE, 2-CHLOROPROPIONATE AND 3-CHLOROPROPIONATE ANIONS

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67-15,795

HACH, Jr., Edwin Ellison, 1934-

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University of New Hampshire, Ph.D., 1967
Chemistry, physical

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B. S., Clarion State College, 1959

A THESIS

Submitted to the University of New Hampshire
In Partial Fulfillment of
The Requirements for the Degree of
Doctor of Philosophy

Graduate School
Department of Chemistry
January, 1967

This thesis has been examined and approved.

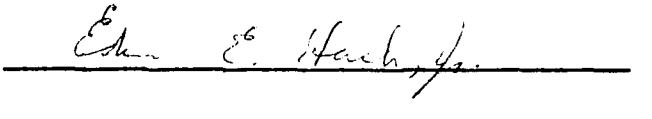
23 March 67
Date

ACKNOWLEDGMENTS

The author first wishes to express his sincere appreciation to the following individuals for their invaluable assistance in the completion of this work: Dr. Charles M. Wheeler for suggesting the problem and possible approaches to its solution, as well as furnishing the guidance and exhortation required to pursue this solution; Dr. Alexander R. Amell for many helpful conversations; Dr. Albert F. Daggett for many helpful discussions and specifically for suggesting the technique used to determine the concentration of excess perchloric acid in the indium stock solutions; Dr. Helmut M. Haendler for many helpful conversations; Dr. David W. Ellis for several helpful suggestions; and Dr. John R. Sabin for his excellent glass blowing in the preparation of the E.M.F. cell.

Also, the author wishes to express his gratitude to the faculty of the Department of Chemistry of the University of New Hampshire for their excellent instruction and the financial aid supplied through the Pratt Grant.

Finally, the author is indebted to the National Science Foundation for its financial support of this research in the summers of 1965 and 1966, through the Summer Fellowship for Teaching Assistants program.



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LIST OF SYMBOLS

C_M	the total metal ion concentration
[M]	the free metal ion concentration
C_A	the total ligand ion concentration
[A]	the free ligand ion concentration
$\bar{n}$	the ligand number
$[H^+]$	the free hydrogen ion concentration
C_S	the concentration of excess perchloric acid in the metal ion solutions
a	an arbitrary quantity by which C_A must be multiplied to give the total ligand acid concentration
f_n	the fraction of the metal ion present in the nth complex
β_n	the overall stability constant for the nth complex
K_n	the stepwise stability constant for the nth complex
$X \equiv$	$(1 + \sum_{n=1}^{N} \beta_n [A]^n)$
$X_n =$	f(X), which is convenient for the graphical evaluation of β_n

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INTRODUCTION

The purpose of this study was to determine the stepwise stability constants and the overall stability constants of certain indium(III) ion complexes. The three ligands employed were the chloroacetate, 2-chloropropionate, and 3-chloropropionate ions. It was anticipated, after examination of the results of a similar study[1], that a correlation between the derived stability constants and acid dissociation constants might be observed.

The original intention was to use a direct polarographic technique for this study. There are, however, certain difficulties in applying this method to the determination of indium(III) ion stability constants. The fundamental problem, with regard to the polarographic method, is the inability to obtain a reversible wave in a solution in which uncomplexed indium(III) ion is the predominant species. More specifically, the reversible polarographic wave is not observed in indium(III) ion solutions in which the pH is low enough to prevent the formation of any preliminary hydrolytic products. This situation, reported by Kolthoff and Lingane[2], and observed by others[3,4], invalidates the normally employed direct method of stability constant determination. Cozzi and Vivarelli[5] have suggested a device for circumventing this experimental difficulty and a similar method was used by Vinogradova and Ching-Ju.[6] In both of these cases a half wave potential value was obtained that purported to represent the uncomplexed indium(III) ion half wave potential. Wheelwright, Spedding and Schwarzenbach[7] have described an indirect polarographic technique for the determination of indium(III) ion stability constants. There

would, however, appear to be some doubt that the polarographic technique is the best choice for a study of the present type.

A potentiometric method, very similar to that employed by Sunden[1], was adopted for this work. Fundamentally, it involved the use of a working half cell, fitted with a quinhydrone-gold electrode, containing the indium(III) ion in acidified perchlorate solution. The ligand solution, in all cases a weak acid in buffered solution, was added to the metal ion solution, and the corresponding electromotive force values were observed. The reference half cell consisted of a quinhydrone-gold electrode in 0.020 M perchloric acid solution. The cell junction was made through a salt bridge of rather intricate design that will be described presently. All determinations were made at 25.00 $\pm$ 0.01°C and at a total ionic strength of 2 M. The e.m.f.'s obtained lead, through the use of certain secondary concentration variables, to overall stability constants for the various complex species appearing in the complex formation process. The overall stability constants obtained readily yield values for the stepwise stability constants.

There are experimental complications, or at least potential complications, that accompany the use of the above technique. One of these results from the use of the metal-quinhydrone electrode. Janz and Ives[8] discuss many of the intrinsic difficulties encountered in the use of this electrode. In a study of the present type, there is, of course, the possibility of indium(III) ion-quinhydrone complex formation. Preliminary work reported by Sunden[1] seems to preclude this.

An additional complication that could result is the formation of polynuclear complexes, which is not uncommon in the case of ions like indium(III). This is particularly so in

the presence of ligands that may act as chelating agents. The ligands involved in this study could conceivably exhibit bidentate behavior. There is a relatively simple experimental procedure available for the detection of polynuclear complex formation in a study of this type. It has been demonstrated[9] that the secondary concentration variable $\bar{n}$ (cf., p. 6) is a function of the free ligand concentration in mononuclear complexes. In polynuclear complexes $\bar{n}$ becomes a function of both the free ligand concentration and the total concentration of metal ion.[10] In the present study, determinations were carried out at three different total metal ion concentrations for each of the ligand systems.

A final complication which must be considered in a study involving indium(III) ion is that of metal ion hydrolysis. Indium(III) ion is known to hydrolyze extensively, and products will begin to precipitate from aqueous solutions at a pH of about 4.[11] It is necessary to avoid this hydrolytic effect, as it would seriously alter the derived stability constants. The indium(III) ion stock solutions were suitably acidified and the ligand buffer solutions were all prepared at a pH less than 4. A relatively simple experimental technique is available to indicate the presence or absence of metal ion hydrolysis. When hydrolysis occurs the quantity $\bar{n}$, which was previously indicated to be a function of the free ligand concentration, also becomes a function of the free hydrogen ion concentration.[12,13] In order to examine this possibility, determinations were carried out at two acid-to-anion ratios for each system.

The experimental and interpretative methods used in

this study have been developed by Bjerrum, Leden, and Fronaeus.* They are summarized by Sunden[1] and elaborated by Rossotti and Rossotti[14] in greater detail. The notation to be adopted in the subsequent discussion is essentially that used by Sunden.[1] It is as follows:

$C_M \equiv$ the total metal ion concentration,

$[M] \equiv$ the free metal ion concentration,

$C_A \equiv$ the total ligand ion concentration,

$[A] \equiv$ the free ligand ion concentration,

$\bar{n} \equiv$ the ligand number; i.e., the number of ligands bound to each central ion,

$[H^+] \equiv$ the free hydrogen ion concentration,

$C_S \equiv$ the concentration of free perchloric acid in the metal ion solutions.

The final quantities obtained from the interpretative procedure are the overall stability constants for the stepwise formation of the complexes (β_n). For the reaction

$$M + nA \rightleftarrows MA_n , \qquad (1)$$

in which there is no polynuclear complex formation, β_n is

*The original development of this material is found in the dissertations of these individuals, and is not readily available to the author: J. Bjerrum, Dissertation, Copenhagen, 1941; I. Leden, Dissertation, Lund, 1943; and S. Fronaeus, Dissertation, Lund, 1948.

defined as

$$\beta_n = \frac{[MA_n]}{[M]\,[A]^n} \qquad 1 \leq n \leq N. \tag{2}$$

In expressions (1) and (2)

$[MA_n] \equiv$ the concentration of the nth complex,

[M] and [A] $\equiv$ the concentration of the metal ion and the ligand, respectively, and

$N \equiv$ maximum coordination number.

The relationships required to interpret the experimental data are developed in the following discussion. It can be seen that

$$C_M = [M] + \sum_{n=1}^{N} [MA_n] , \tag{3}$$

and substituting from (2)

$$C_M = [M]\ (1 + \sum_{n=1}^{N} \beta_n [A]^n). \tag{4}$$

Likewise

$$C_A = [A] + \sum_{n=1}^{N} n[MA_n] = [A] + [M] \sum_{n=1}^{N} n\beta_n [A]^n. \tag{5}$$

In order to simplify, consider that

$$X \equiv (1 + \sum_{n=1}^{N} \beta_n [A]^n) \ ; \tag{6}$$

then

$$C_M = [M]\ X. \tag{7}$$

Noting that

$$\frac{dx}{d[A]} = \sum_{n=1}^{N} n\beta_n\ [A]^{n-1}\ , \tag{8}$$

it can be seen that

$$C_A = [A] + [M]\,[A]\ \frac{dx}{d[A]}\ . \tag{9}$$

The number of ligands bound to each central ion, $\bar{n}$, may be defined as

$$\bar{n} = \frac{C_A - [A]}{C_M}\ . \tag{10}$$

Substituting from (7) and (9),

$$\bar{n} = \frac{dx\ [A]}{X\ d[A]}\ ; \tag{11}$$

rearranging

$$\frac{dX}{X} = \frac{\bar{n}}{[A]}\ d[A]_j; \tag{11a}$$

and integrating leads to

$$\ln X = \int_0^{[A]} \frac{\bar{n}}{[A]}\ d[A]\ . \tag{12}$$

The quantity X may thus be determined by measurement of [A].

The overall stability constant, β_n, may then be obtained from X. Consider now the experimentally measurable quantities and their relationship to [A] and finally, X.

A competitive system is established in the working electrode compartment in the course of the titration operation. The indium(III) ions and protons compete for the weak acid anions. The progress of this competition can be observed empirically by measuring the free hydrogen ion concentration with a suitable probe electrode. The glass electrode is not a suitable probe in this study. Rossotti and Rossotti[15] have indicated that the glass electrode exhibits erratic behavior in the presence of highly charged cations such as the indium(III) ion. Some preliminary work in this laboratory seems to bear this out. The quinhydrone electrode appeared to be the most attractive of the remaining possibilities. The e.m.f. values related to the hydrogen ion concentrations established in the probe electrode compartment are defined as follows:

$E \equiv$ e.m.f. of the cell containing the complex solution, where the hydrogen ion concentration = $[H^+]$,

$E_o \equiv$ e.m.f. of the same cell with $C_M = 0$, where the hydrogen ion concentration = $[H^+]_o$,

$E_A \equiv E_o - E$ the potential difference between the half cell containing only the ligand buffer solution and that containing the complex solution.

The expressions obtained in the following discussion are based on millimolar concentrations and a temperature of 25°. It must be noted also that the concentration of perchloric acid in the reference half cell was 0.020 M.

$$E_A \equiv E_o - E = 59.17 \log \frac{[H^+]}{[H^+]_o} \quad (13)$$

(note: $\frac{2.303\ RT}{nF} = 59.17$)

$$K_a = \frac{[H^+]\,[A]}{aC_A + C_S - [H^+]} = \frac{[H^+]_o(C_A + [H^+]_o)}{aC_A - [H^+]_o} \quad (14)$$

Equation (14) results from application of the law of mass action to the dissociation of the weak acids used in the ligand solutions and the observation that the concentration of undissociated acid, HA, may be expressed as $aC_A + C_S - [H^+]$ in the metal ion solution and as $aC_A - [H^+]_o$ in the buffer solution alone. It is also necessary to recognize that $(C_A + [H^+]_o)$ represents the acid anion concentration in the buffer solution alone. The quantity a, which appears in equation (14) and throughout the remainder of this report, is an arbitrary quantity for each of the ligand systems. It represents the number by which C_A must be multiplied to yield the total ligand acid concentration. Combining equations (13) and (14) leads to

$$E_A = 59.17 \log \left(\frac{C_A + \frac{C_S}{a} - \frac{[H^+]}{a} + (1 + \frac{1}{a})[H^+]_o}{[A]} \right) , \quad (15)$$

which may be rearranged to

$$\log [A] = \log \left(C_A + \frac{C_S}{a} - \frac{[H^+]}{a} + (1 + \frac{1}{a})[H^+]_o\right) - \frac{E_A}{59.17} . \quad (15a)$$

$[H^+]$ and $[H^+]_o$ values may be obtained from

$$E = 59.17 \log \frac{20.0}{[H^+]} \quad (16)$$

or

$$\log [H^+] = \log 20.0 - \frac{E}{59.17} , \quad (16a)$$

and the other quantities necessary for the calculation of [A] by equation (15a) are known from the titration data. In a competitive system of this type it can be seen that a valid expression for the ligand number, $\bar{n}$, is

$$\bar{n} = \frac{C_A + [H^+] - C_S - [A]}{C_M} \qquad (17)$$

as $C_A + [H^+] - C_S$ is an adequate representation of the total ligand ion concentration. When [A] has been calculated from the above relationships, all the quantities necessary for the determination of $\bar{n}$ are available. The integral in equation (12) may now be evaluated graphically by plotting the quotient $\frac{\bar{n}}{[A]}$ as a function of [A]. Graphical integration yields values of X for the values of the free ligand concentration chosen as the limits of integration ($[A]_j$). An examination of the $\frac{\bar{n}}{[A]}$ vs. [A] curve, which is obtained from determinations with three different series of total metal ion concentrations and two different acid to anion buffer ratios, will indicate if either polynuclear complex formation or metal ion hydrolysis effects do exist.

A graphical procedure may also be used to determine the overall stability constants. In order to do this a new quantity, X_1, is defined as

$$X_1 = \frac{(X - 1)}{[A]} \; ; \qquad (18)$$

substituting equation (6) into equation (18) gives

$$X_1 = \sum_{n=1}^{N} \frac{\beta_n [A]^n}{[A]} = \beta_1 + \beta_2 [A] + \beta_3 [A]^2 + \ldots\ldots \qquad (18a)$$

Values of X_1 calculated by equation (18) may then be plotted as a function of [A] and the intercept at [A] = 0 taken as β_1.

Then by defining a second new quantity, X_2, as

$$X_2 = \frac{(X_1 - \beta_1)}{[A]} = \beta_2 + \beta_3[A] + \beta_4[A]^2 + \ldots\ldots \quad (19)$$

and proceeding as described above, β_2 may be determined. This process may be repeated for all values of β_n through the maximum experimental coordination number and in general results in relationships of the type

$$X_n = \frac{(X_{n-1} - \beta_{n-1})}{[A]} = \beta_n + \beta_{n+1}[A] + \beta_{n+2}[A]^2 + \ldots. \quad (20)$$

In practice the final stability constant, symbolized as β_m, (m = 4 to 6 in the systems studied here) was obtained by drawing the best straight line through the points from

$$X_n = \beta_n + \beta_m[A] + \ldots\ldots \quad (21)$$

and taking the slope as β_m. This can be done without requiring extremely severe graphical approximations, and was a necessary consequence of the reduced number of values for X_n which came out of the calculations.

The overall stability constants for the stepwise formation of the complexes (β_n's) can be readily converted to stepwise stability constants (K_n's). The stepwise stability constant, K_n, is defined for the reaction

$$MA_{(n-1)} + A \gtrless MA_n \quad (22)$$

as

$$K_n = \frac{[MA_n]}{[MA_{(n-1)}][A]} \quad (23)$$

Recalling the defining terms for the overall stability con-

stants (equations (1) and (2)) it can be readily seen that

$$\beta_n = \prod^{n} K_n \cdot \tag{24}$$

Both sets of constants are reported in this study.

EXPERIMENTAL

The determination of stoichiometric stability constants must be performed in a manner such that the activity coefficients of the complex forming species remain essentially constant. If this is not the case, the concentration quotients will not represent constant numerical quantities.[16] In the present study the activity coefficients were stabilized by maintaining the ionic strength at a numerical value considerably higher than the concentrations of the complexing materials. All solutions used in the titrations were prepared at a total ionic strength of 2 M, with sodium perchlorate as a bulk electrolyte.

All determinations were carried out at 25.00 $\pm$ 0.01°C.

Materials

Sodium perchlorate. Purified grade sodium perchlorate was recrystallized twice from hot water and dried at 100°C.[17] The chloride and chlorate ion content were negligible.

Indium perchlorate. Indium perchlorate (G. F. Smith Co.) was dissolved in water and precipitated with 6 M ammonium hydroxide as indium hydroxide. The indium hydroxide was washed thoroughly with water and redissolved in an aqueous solution of perchloric acid. This stock solution was analyzed gravimetrically for indium by the method described by Busev.[18]

The determination of the excess perchloric acid concentration in the stock solution presented a problem. An acid-base titration in the presence of indium(III) ion in a non-complexing solution results in the precipitation of indium(III) hydroxide at a pH of about 4. In order to avoid this, a known

volume of stock solution was passed through an ion exchange column packed with acidified, washed Dowex 50 cation exchange resin. Dowex 50 quantitatively exchanges hydrogen ion for indium(III) ion. The resulting eluate was titrated potentiometrically in triplicate with standardized, carbonate free sodium hydroxide. The excess acid concentration was calculated by comparing the results of this titration with the gravimetrically determined indium(III) ion concentration.

Perchloric acid. Baker and Adamson, reagent grade.

Quinhydrone. Fisher quinhydrone (m.p. 170-172°) gave results in very good agreement with those obtained with quinhydrone purified by the procedure of Harned and Wright.[19] The Fisher quinhydrone exhibited somewhat greater stability, with respect to the e.m.f. measurements, and was used throughout this study.

Monochloroacetic acid. Fisher, certified reagent grade.

2-Chloropropionic acid. Aldrich, research grade, $n_D^{20} = 1.4330$, b.p. 186°.

3-Chloropropionic acid. Eastman, Eastman grade, m.p. 40-42°.

Sodium hydroxide. Fisher certified reagent grade.

Water. Distilled water which had been passed through a two-chamber deionizer was used for the preparation of solutions and washing operations. This water was frequently monitored for chloride ion with no positive results.

Nitrogen. Nitrogen gas used in this investigation was passed over hot copper turnings to remove oxygen and then dried by passage through concentrated sulphuric acid.

Apparatus

Potentiometer. Rubicon Co. of Philadelphia, Pa., serial number 43113.

Galvanometer. G-M Laboratories Inc., Chicago, Ill, catalog number 570-402.

Standard cell. The cell used was a certified Weston Cell of the low temperature coefficient type. It was manufactured by Eppley Laboratories Inc., Newport, R. I.

E.M.F. cell. The basic design of the cell used for the e.m.f. measurements was developed by Forsling, Hietanen and Sillen.[20] This type of cell and its merits are discussed by Rossotti and Rossotti.[21] The cell, shown as Fig. 1, has been modified slightly from the original version of Forsling et. al. Compartment A represents the reference electrode chamber and D, the working electrode chamber. The segments B and C depict the salt bridge. Section B of the salt bridge was mounted in the constant temperature bath throughout a series of determinations, whereas section C was removed with the compartment D after each determination. The flexibility imparted by the short piece of tygon tubing, L, was of great advantage in removing and replacing section C. Reservoir E of the salt bridge was filled with the reference electrode solution. Reservoir F was filled with the bridge electrolyte, 2 M sodium perchlorate. This type of salt bridge was well suited to the performance of a series of determinations as it was possible to renew the liquid junction, occurring at stopcock H, after each determination. This was done by appropriate manipulation of stopcocks G, H and I. The ligand was added to the reaction chamber from the offset buret M.

In a cell of this type it is necessary to determine

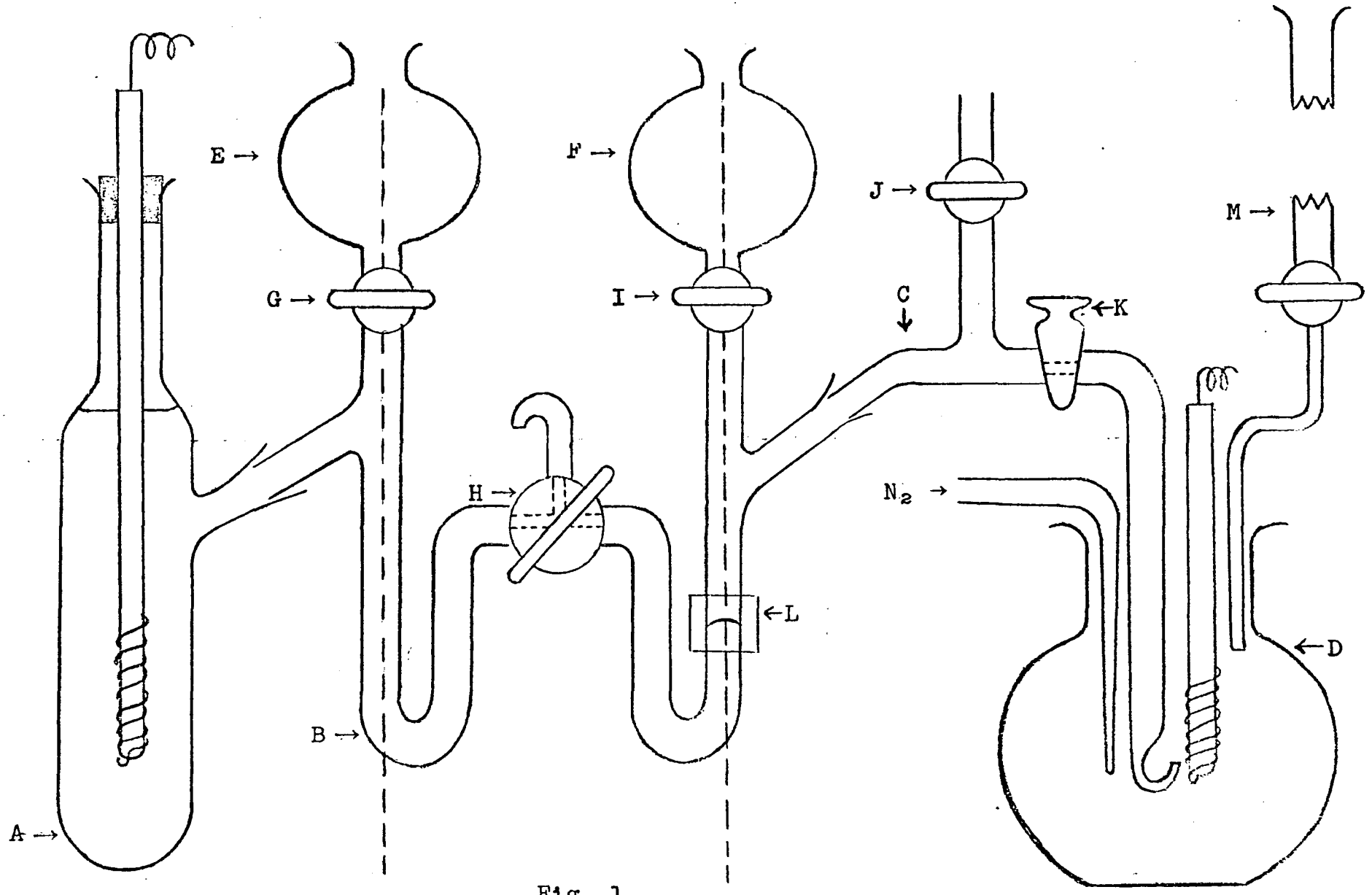

Fig. 1

E.M.F. Cell

the consequence, if any, of the liquid junction. This can be done by observing the effect of bridge electrolyte concentration on the measured e.m.f.'s. As noted by Rossotti and Rossotti[21], the measured cell potential is not a function of the bridge electrolyte concentration if the junction potential has been eliminated. E.m.f. measurements were made with this cell at three different bridge electrolyte concentrations. The three concentrations were 0.5 M, 2 M and 4 M, and the electrolyte used was sodium perchlorate. The extremely slight differences observed in the e.m.f.'s at the three concentrations were less than the uncertainty found in previous and subsequent measurements. The junction potential was, therefore, considered insignificant.

Gold electrodes. Both Sargent number 30435 and Leeds and Northrup number 7701 gold electrodes were used. Of these two types, the Leeds and Northrup electrode may be slightly superior for this type of work, both in terms of durability and potential fidelity.

pH meter. Beckman Zeromatic, model 9602.

Procedures

Sample preparation in the working half cell. Many investigators[19,22,23] have indicated the necessity of excluding oxygen in the preparation of quinhydrone half cells. All working half cells were prepared and kept under a nitrogen atmosphere until the period immediately prior to the titration operation. The preparative work was done in a large dry box which had been well flushed with nitrogen. A slight positive nitrogen pressure was maintained in the dry box at all times. A 75 ml sample of 2 M sodium perchlorate solution (for the E_o values) or metal ion solution (for the E values) was pipetted into the reaction electrode compartment, D, in which had previously been placed enough solid quinhydrone to insure a saturated quinhydrone solution. The half cell chamber was stoppered and stored in the nitrogen atmosphere for a period of several hours. The sample was then removed from the dry box and taken to the cell location. Care was taken to avoid unnecessary splashing of the wet quinhydrone onto the reaction chamber above the level of the liquid.

A somewhat similar procedure was used in the preparation of the reference half cell.

Electrode cleaning and preparation. As Janz and Ives[24] point out, there have been many procedures suggested for the preparation of the metal phase of the quinhydrone electrode.[25-29]

The cleaning problem, reduced to its practical aspects, seems to be essentially this: there is an absolute necessity to remove all interfering surface deposits coupled with an equally exigent requirement to maintain the integrity of the rather tenuous gold-glass seal. After examining several possibilities, the following procedure was adopted: the lower half

of the electrode was immersed in a cold 1:1 nitric acid-water cleaning mixture. The cleaning mixture was heated slowly to 40-45° and maintained at this temperature for at least twenty minutes. The electrode and cleaning mixture were then allowed to cool to room temperature. The electrode was washed successively with distilled water, deionized water containing a trace of ammonia, and finally deionized water. The electrode was immersed in deionized water until just prior to its use in a titration. At that time it was rinsed again with deionized water and immersed in a tube of deionized water. Then it was rinsed with deionized water, immersed in a tube of absolute ethanol, and finally placed in a 250 ml side arm flask fitted out as a nitrogen drying chamber. The electrode was suspended in the nitrogen stream for at least twenty minutes, which was sufficient for complete drying in all cases. At this point, the electrode was placed in the working half cell. The initial part of this cleaning procedure was suggested fundamentally by Leeds and Northrup in an instruction pamphlet that accompanied their electrodes. The latter phases of the cleaning operation are very similar to the technique developed by Morgan, Lammert and Campbell.[27]

The other facet of electrode preparation that had to be considered was that of electrode aging or equilibration in the reaction compartment solution. Some attention has been given to this aging process in previous studies[27,30-33], and it has been discussed in certain works dealing with electrode preparation and evaluation.[8,34] A cleaned, dry electrode was immersed in the reaction half cell compartment in such a way that the gold portion of the electrode was in contact with some of the excess quinhydrone.[34] The electrode remained immersed in the half cell solution for a period of at least 60 min. before the titration was begun. During this period a

gentle stream of nitrogen was continuously passed through the solution.

Electrode standardization. It was necessary to use a number of the gold electrodes to complete the series of determinations in the reaction chambers, and a gold electrode was used in the reference half cell as well. It seemed desirable, therefore, to establish some type of electrode standardization procedure. A technique very similar to that employed by Morgan, Lammert, and Campbell[27] was adopted. Four of the probe electrodes and the reference electrode were immersed in approximately 0.1N perchloric acid solution which was saturated with quinhydrone. After a 90 min. equilibration at 25.00°C, the electrodes were connected in pairs and the e.m.f. of each pair was observed. Nitrogen gas was passed through the cell continuously throughout the measurements, as well as during the equilibration period. Two series of readings including all possible electrode tandem arrangements were made. In the first series the maximum e.m.f. difference measured was 0.00003 V. In the second series there was no observable e.m.f. difference. Precautions similar to those delineated in the discussion of working half cell preparation were taken in the preparation of this cell. Figure 2 is a representation of the cell arrangement used in the electrode standardization procedure.

Potentiometric titrations. The titrations were begun immediately after the electrode aging process was completed. The ligand buffer solution was added to the reaction electrode compartment in predetermined portions. The solutions were mixed by an appropriate stream of nitrogen which had been prehumidified by passage through a 2 M sodium perchlorate solution immersed in the constant temperature bath. The e.m.f. values were attained almost immediately and were quite stable.

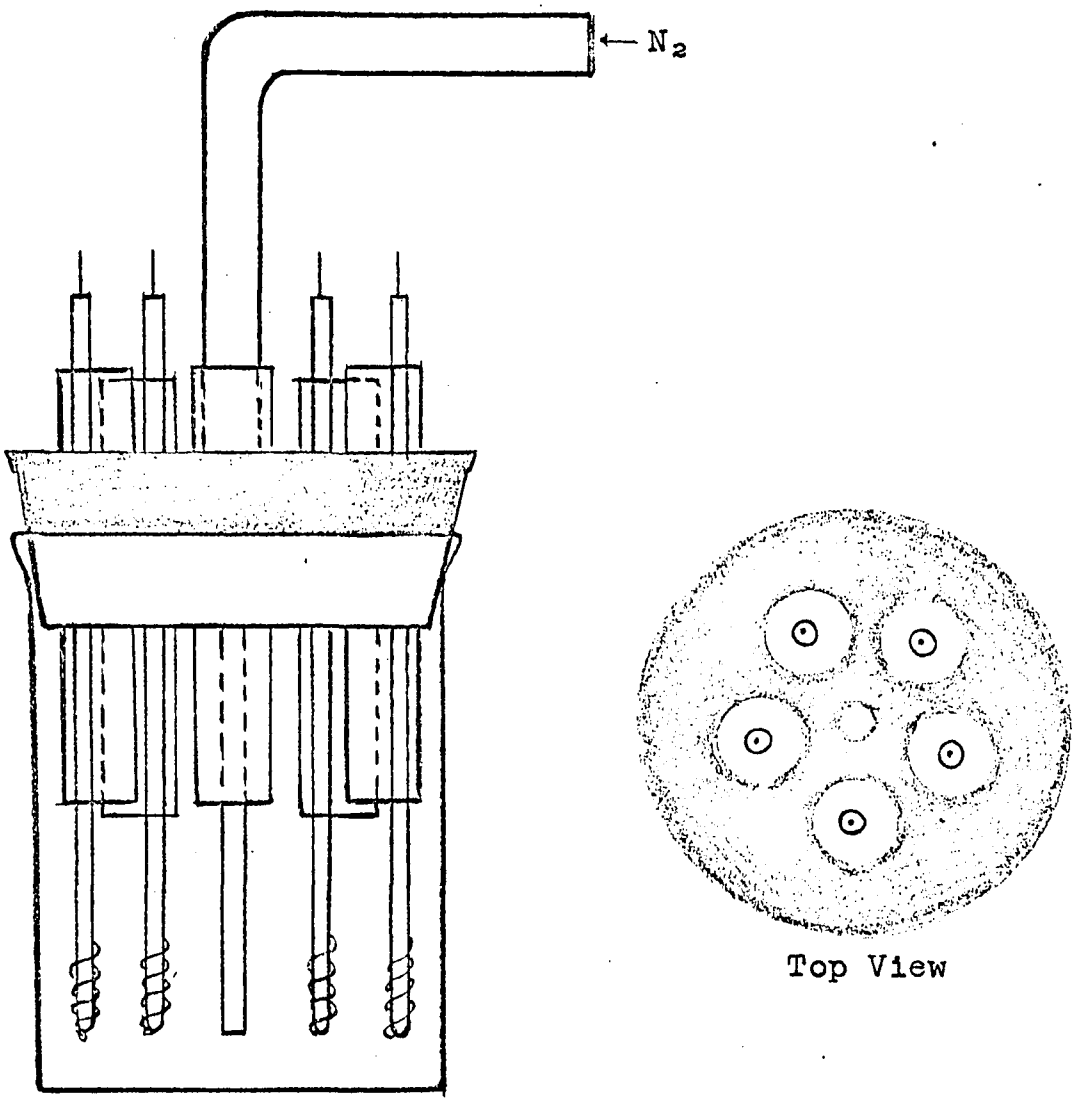

Fig. 2.

Electrode Standardization Cell

The null point was usually found at least four times for each e.m.f. measurement and the readings differed by 0.02 to 0.05 mV. The reproducibility of the e.m.f. measurements was generally $\pm$ 0.4 mV for the chloroacetate and 3-chloropropionate systems and $\pm$ 0.2 mV for the 2-chloropropionate system.

The cell composition was very similar to that described by Sunden[1], and may be represented as follows:

		C_M mM $In(ClO_4)_3$,
20 mM $HClO_4$,		C_A mM NaA,
Au ; 1980 mM $NaClO_4$,		aC_A mM HA, ; Au
Quinhydrone		(2000 - 6 C_M - C_A) mM $NaClO_4$,
		Quinhydrone

in which

A $\equiv$ chloroacetate, 2-chloropropionate, or 3-chloropropionate anion

a = 4 and 1 for the chloroacetate system

a = 3 and 1 for the 2- and 3-chloropropionate systems

The left side of the above representation describes the reference electrode that was used. As has been stated previously, the solution in the working half cell (right side of the cell representation) was the result of mixing the ligand solution with the metal ion solution. In general, the initial concentrations (before mixing) of the ligand and metal ion solutions may be described as follows:

Ligand Solutions	Metal Ion Solutions
a·1000 mM HA	N_M mM $In(ClO_4)_3$
1000 mM NaA	(2000 - 6 N_M) mM $NaClO_4$
1000 mM $NaClO_4$	

in which N_M represents the concentration of the metal ion, 0, 10, 20 and 40 for each system. The quantities C_A and C_M varied throughout a titration, and these concentrations were calculated on the basis of the known volumetric relationships and the initial concentrations. There were three sets of C_M values for each system corresponding to the three different initial metal ion concentrations. The e.m.f. values obtained when $N_M = 0$ were the E_o values, which have been defined previously. A complete set of determinations for any of the ligand systems would consist of determinations where $a = 4$, $N_M = 0$; $a = 4$, $N_M = 10$; $a = 4$, $N_M = 20$; and $a = 4$, $N_M = 40$. There would also be a determination in which $a = 1$ at one of the initial metal ion concentrations. The initial metal ion concentration chosen in all systems was 20 mM.

Preparation of the ligand buffer solutions. Two problems were encountered in the preparation and use of the ligand buffer solutions.

The first was the lack of sodium salts of the acid of the required purity. The sodium salts were prepared, therefore, in situ, by a method quite similar to that of Ahrland.[35] A suitable quantity of acid was weighed out and dissolved in a limited amount of water. Then a predetermined quantity of standardized, carbonate free sodium hydroxide was added to neutralize the required amount of acid. Upon addition of the necessary amount of sodium perchlorate, the resulting solution was diluted to the appropriate volume.

The second difficulty resulted from the tendency of these chlorosubstituted acids to hydrolyze in water solutions forming the hydroxyacids.[36] Preliminary experimentation with chloroacetic acid, in which the progress of the hydrolysis was monitored by means of silver chloride precipitation, indicated that the hydrolysis progressed rather slowly. Ligand solutions made freshly every day proved to be quite satisfactory. This was borne out experimentally by comparing the e.m.f.'s of identical determinations in which the first determination was carried out with a one day old sample of ligand solution and the second determination was carried out with a freshly prepared ligand solution. The e.m.f. values from the two determinations agreed well within the limits of reproducibility.

The hydrolysis appeared to occur somewhat more rapidly in both the 2- and 3-chloropropionic acids. The ligand solution for each determination involving these acids was prepared immediately prior to the determination. The obvious problem in a situation of this type was that of exactly reproducing the ligand solution for the various determinations. Very stringent mechanical operational limits were required, and this precaution was observed. Also an attempt was made to establish a standardization criterion for these solutions. A rapid check of ligand solution pH was made on each new sample. The pH values so observed always agreed within 0.1 of a pH unit for the "same" ligand solution. This standardization procedure, if it may be called that, is admittedly a poor one in solutions of this type. It has only rapidity to commend it. It is of interest to note, however, that the degree of reproducibility attained in the potentiometric titrations does seem to indicate that essentially the "same" ligand solution was used where required.

An additional experimental technique was used to assess the effect of any hydrolysis on the observed e.m.f's A sample of the ligand solution for the 2-chloropropionate system was made up and 50 ml of this solution was introduced immediately into a properly prepared sample of metal ion solution. The ligand solution at this time exhibited no positive test for chloride ion, indicating the absence of acid hydrolysis. The 50 ml of ligand solution represented the total volume of ligand added in a previous, identical, stepwise titration. The e.m.f. measurement taken on immediate addition of 50 ml of ligand was compared with the final e.m.f. measurement from the stepwise titration. This comparison indicated that the formation of the hydroxyacid, with the attendant introduction of chloride ions during the course of a normal, stepwise titration, may be considered an unimportant effect.

DISCUSSION

Results

Monochloracetate system. The data for the chloroacetate system have been summarized in Table I. All e.m.f. values shown in this table are averages. [A] was calculated by means of equation (15a) after $[H^+]$ and $[H^+]_o$ were obtained from equation (16a). C_S values are necessary for equation (15a), and were obtained as a result of the excess acid analysis of the indium(III) ion stock solution; $C_S = 0.162\ C_M$. The calculations of $\bar{n}$ values were accomplished by equation (17).

The integral, $\int_o^{[A]_j} \frac{\bar{n}}{[A]} d[A]$ of equation (12), was evaluated graphically; Figures 3 and 4. In Figure 3 the initial portions of the abscissa are represented in an expanded scale to facilitate the extrapolation to [A] = 0. The points from the three different metal ion concentrations and the two different acid to anion ligand buffer ratios all fall on essentially the same curve. The points approach the curve within the accidental error associated with the determinations. This indicates that polynuclear complex formation and metal ion hydrolysis are insignificant effects.

The graphical integration was done with a planimeter. All areas were circumscribed at least three times and the average value was used. The limit of integration, $[A]_j$, was chosen as:

$$[A]_j = 1,5,10,20,50,100,\ 200,\ 300,\ \text{and}\ 400\ \text{mM}$$

The results of the integration are shown in Table II along

TABLE I

DATA SUMMARY FOR THE CHLOROACETATE SYSTEM

($C_S = 0.162\ C_M$)

Total Metal Ion Conc., C_M / mM	Total Ligand Conc., C_A / mM	E_o* / mV	E / mV	E_A (E_o -E) / mV	Free Ligand Conc., [A] / mM	$\bar{n}$/[A] / 1/M
	Buffer: Chloroacetic acid/Chloroacetate = 4/1					
9.87	13.16	39.28	23.10	16.18	9.03	116.7
9.62	38.46	34.47	24.00	10.46	28.91	57.00
9.38	62.50	33.45	25.48	7.96	49.76	39.93
9.15	85.36	33.05	26.54	6.51	70.53	31.72
8.82	117.6	32.90	27.76	5.14	100.8	24.92
8.33	166.7	33.10	29.04	4.06	147.1	20.16
7.89	210.5	33.40	30.08	3.32	189.8	17.11
7.50	250.0	33.76	30.96	2.80	229.2	14.88
7.14	285.7	34.13	31.60	2.52	264.0	14.00
6.82	318.2	34.50	32.26	2.23	296.7	12.90
6.52	347.8	34.85	32.85	2.00	326.7	12.02
6.00	400.0	35.58	33.86	1.71	379.2	11.07

continued-

*E = e.m.f. when $C_M = 0$

TABLE I-2

Total Metal Ion Conc., C_M mM	Total Ligand Conc., C_A mM	E_o* mV	E mV	E_A (E_o -E) mV	Free Ligand Conc., [A] mM	$\bar{n}$/[A] 1/M
19.74	13.16	39.28	12.32	26.96	5.70	148.1
19.23	38.46	34.47	14.91	19.56	20.08	68.52
18.75	62.50	33.45	18.22	15.23	37.38	45.53
18.29	85.36	33.05	20.66	12.39	56.04	34.44
17.65	117.6	32.90	23.07	9.82	84.05	26.17
16.67	166.7	33.10	25.62	7.48	128.9	19.77
15.80	210.5	33.40	27.36	6.04	170.9	16.27
15.00	250.0	33.76	28.66	5.10	209.7	14.12
14.28	285.7	34.13	29.72	4.42	245.2	12.70
13.64	318.2	34.50	30.60	3.89	278.4	11.50
13.04	347.8	34.85	31.34	3.50	308.2	10.80
12.00	400.0	35.58	32.62	2.96	361.3	9.78

*E_o = e.m.f. when C_M = 0

continued-

TABLE I-3

Total Metal Ion Conc., C_M mM	Total Ligand Conc., C_A mM	E_o* mV	E mV	E_A (E_o -E) mV	Free Ligand Conc., [A] mM	$\frac{\bar{n}}{[A]}$ 1/M
39.47	13.16	39.28	1.46**	40.74	3.05	206.9
38.46	38.46	34.47	0.17**	34.64	10.79	100.1
37.50	62.50	33.45	3.94	29.50	21.10	66.35
36.58	85.36	33.05	7.93	25.12	33.89	48.60
35.29	117.6	32.90	12.46	20.43	55.50	35.06
33.33	166.7	33.10	17.49	15.61	93.90	24.76
31.58	210.5	33.40	20.72	12.68	132.1	19.70
30.00	250.0	33.76	23.06	10.70	168.9	16.65
28.57	285.7	34.13	24.84	9.30	203.0	14.77
27.27	318.2	34.50	26.26	8.23	235.2	13.38
26.09	347.8	34.85	27.53	7.32	265.9	12.18
24.00	400.0	35.58	29.42	6.16	319.2	10.87

*E_o = e.m.f. when C_M = 0

**These readings were taken with the polarity of the e.m.f. cell reversed.

continued-

TABLE I-4

Total Metal Ion Conc., C_M / mM	Total Ligand Conc., C_A / mM	E_o* / mV	E / mV	E_A (E_o -E) / mV	Free Ligand Conc., [A] / mM	$\bar{n}$/[A] / 1/M
Buffer: Chloroacetic acid/Chloroacetate = 1/1						
19.74	13.16	71.80	29.88	41.92	2.46	282.9
19.23	38.46	69.18	41.60	27.58	13.78	96.30
18.75	62.50	68.60	48.72	19.88	30.13	57.22
18.29	85.36	68.41	52.70	15.71	48.06	41.97
17.65	117.6	68.32	56.31	12.01	75.81	30.76
16.67	166.7	68.37	59.65	8.72	121.2	22.15
15.80	210.5	68.50	61.65	6.85	163.9	17.70
15.00	250.0	68.61	62.96	5.65	203.5	15.00
14.28	285.7	68.66	63.89	4.77	240.1	13.11
13.64	318.2	68.81	64.62	4.19	273.1	11.95
13.04	347.8	68.94	65.24	3.70	304.0	10.91
12.00	400.0	69.12	66.09	3.03	358.2	9.63

*E_o = e.m.f. when C_M = 0

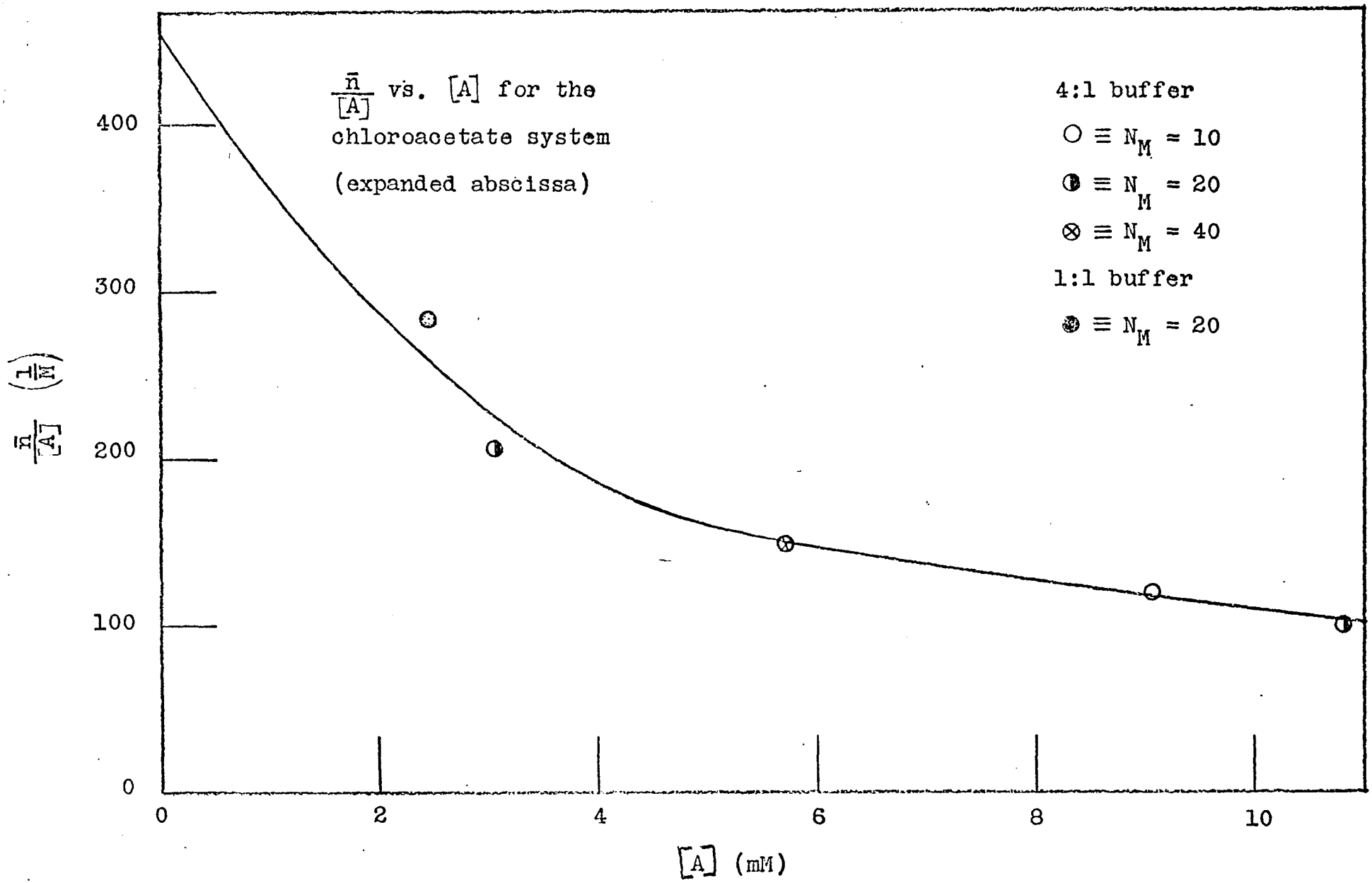
$\frac{\bar{n}}{[A]}$ vs. [A] for the
chloroacetate system
(expanded abscissa)
4:1 buffer
○ ≡ N_M = 10
◑ ≡ N_M = 20
⊗ ≡ N_M = 40
1:1 buffer
◍ ≡ N_M = 20
$\frac{\bar{n}}{[A]}$ $\left(\frac{1}{M}\right)$
400
300
200
100
0
0
2
4
6
8
10
[A] (mM)

Fig. 3

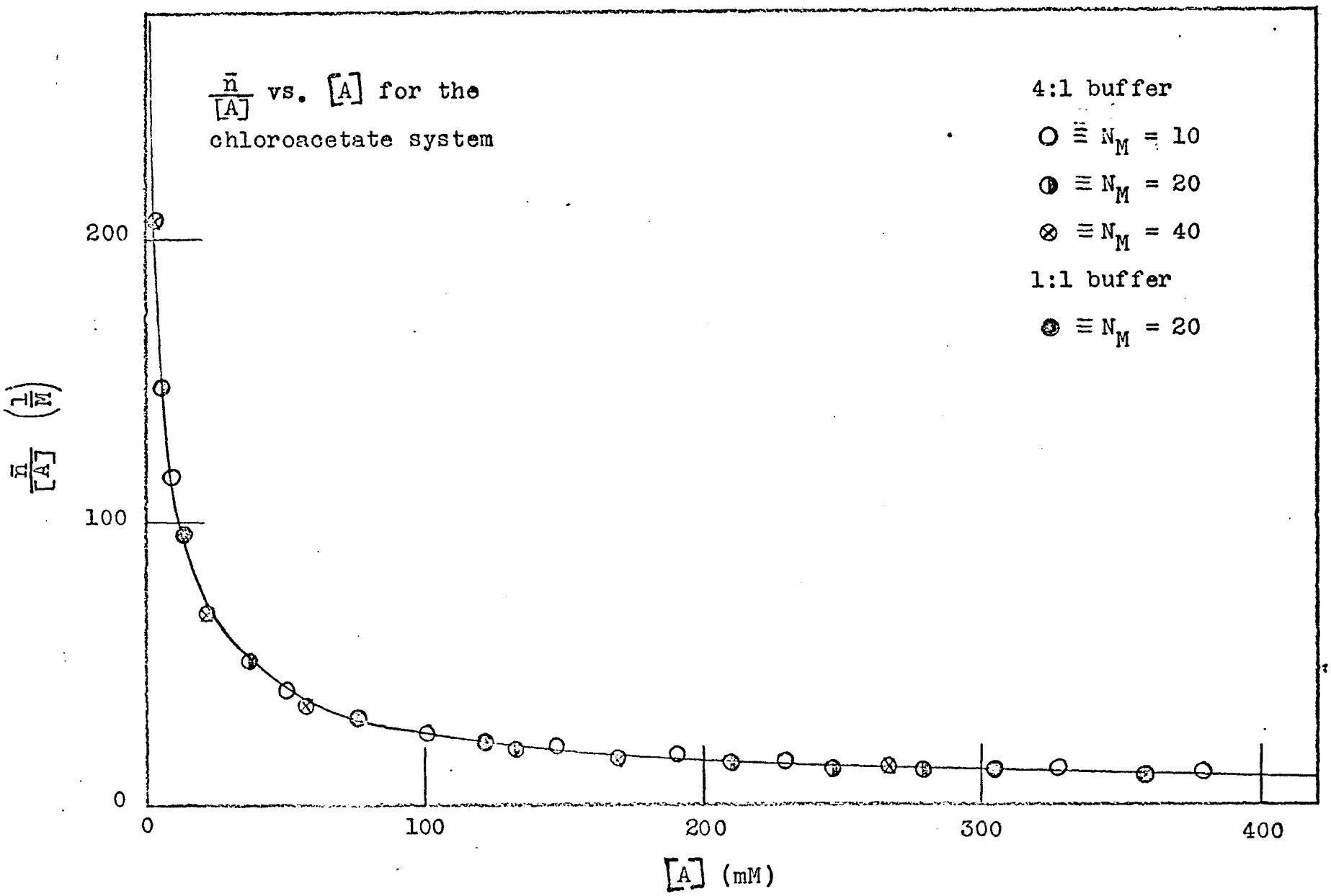
$\frac{\bar{n}}{[A]}$ vs. [A] for the
chloroacetate system
4:1 buffer
○ ≡ N_M = 10
◑ ≡ N_M = 20
⊗ ≡ N_M = 40
1:1 buffer
◉ ≡ N_M = 20
$\frac{\bar{n}}{[A]}$ $(\frac{1}{M})$
200
100
0
0
100
200
300
400
[A] (mM)

Fig. 4

TABLE II

DATA FOR THE DETERMINATION OF THE OVERALL STABILITY CONSTANTS FOR THE CHLOROACETATE SYSTEM

Free Ligand Conc., [A] mM	Ligand Number, $\bar{n}$	$\int_{o}^{[A]_j} \frac{\bar{n}}{[A]} d[A]$	X	X_1 M^{-1}	$X_2 \cdot 10^{-3}$ M^{-2}	$X_3 \cdot 10^{-4}$ M^{-3}
1.0	0.358	0.4012	1.49	490	-	-
5.0	0.765	1.329	3.78	556	-	-
10.0	1.06	1.944	6.98	598	12.8	-
20.0	1.41	2.803	16.5	775	15.2	-
50.0	1.93	4.321	75.2	$1.48 \cdot 10^3$	20.2	-
100	2.30	5.781	324	$3.23 \cdot 10^3$	27.6	17.6
200	3.02	7.570	$1.94 \cdot 10^3$	$9.70 \cdot 10^3$	46.2	18.1
300	3.21	8.804	$6.65 \cdot 10^3$	$2.22 \cdot 10^4$	72.4	20.8
400	3.60	9.747	$1.71 \cdot 10^4$	$4.27 \cdot 10^4$	106	24.0

with related data.

The $\bar{n}$ quantities shown in Table II were obtained graphically (from Figures 3 and 4), and they suggest the maximum coordination number for which these data are meaningful is four. There is, of course, the possibility that extending the range of the titration to higher ligand concentrations might increase the value of $\bar{n}$. This would have the effect of making an additional stability constant or constants available. Reference to Table I, however, casts considerable doubt on this eventuality. When the initial concentration of indium(III) perchlorate was 10 mM the E value approached the E_o value very closely. Also, the change exhibited by the E values on the last four or five additions of ligand, which were significant portions, was relatively small.

The X values were calculated from equation (12) in the form

$$\log X = \frac{\int_0^{[A]_j} \frac{\bar{n}}{[A]}\, d[A]}{2.303} \qquad (25)$$

The X_n values ($n = 1 \rightarrow 3$) were calculated as described in the introduction of this paper, so that

$$X_1 = \frac{(X - 1)}{[A]} = \beta_1 + \beta_2 [A] + \beta_3 [A]^2 + \beta_4 [A]^3$$

$$X_2 = \frac{(X_1 - \beta_1)}{[A]} = \beta_2 + \beta_3 [A] + \beta_4 [A]^2$$

and

$$X_3 = \frac{(X_2 - \beta_2)}{[A]} = \beta_3 + \beta_4 [A]$$

β_1 was determined by finding the intercept [A] = 0 in a plot of X_1 as a function of [A]. This plot is shown in Figure 5.

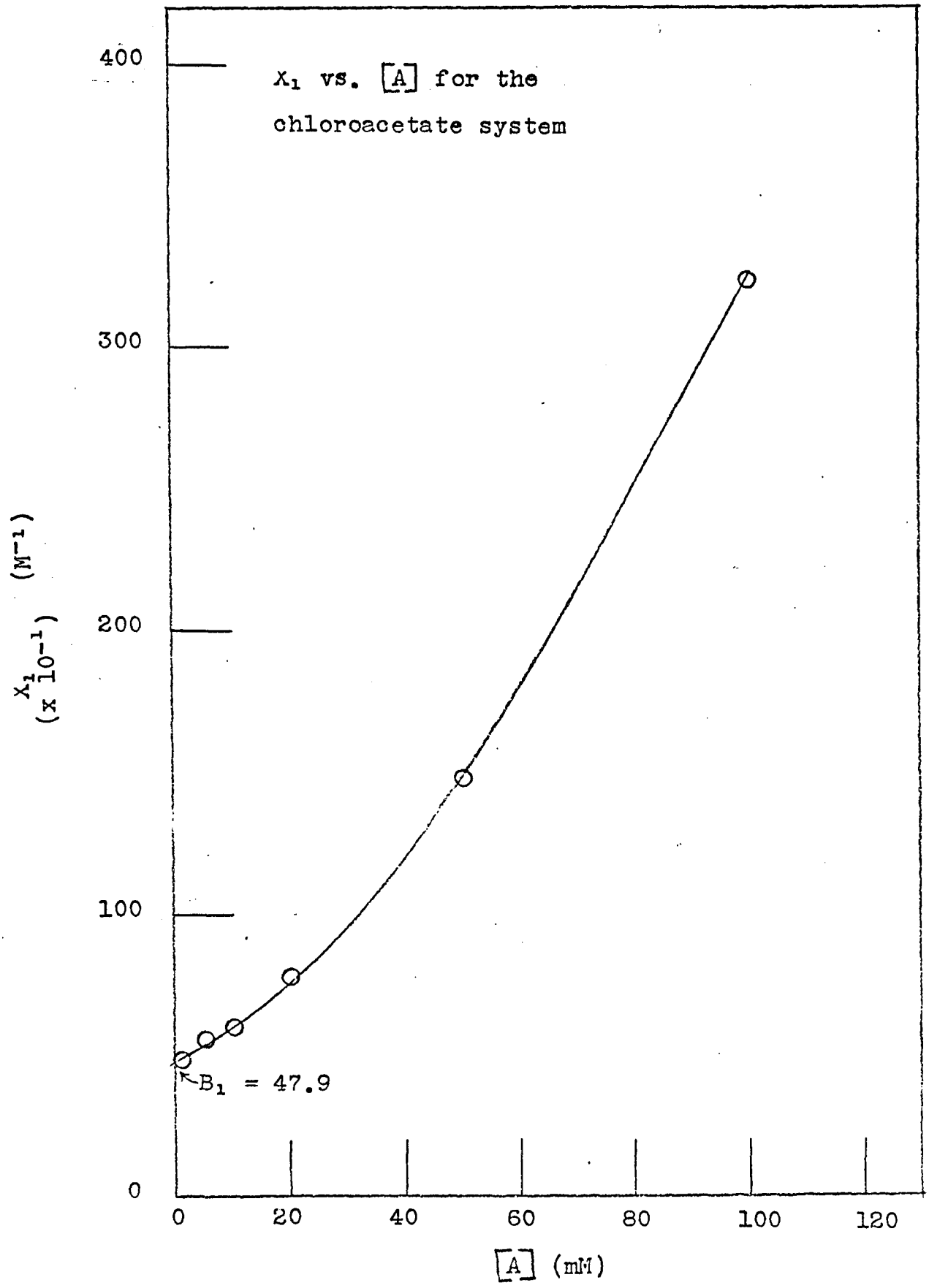
X_1 vs. [A] for the chloroacetate system
400
300
200
100
0
X_1 ($\times 10^{-1}$) (M^{-1})
B_1 = 47.9
0
20
40
60
80
100
120
[A] (mM)

Fig. 5

β_2 and β_3 were determined in exactly the same way and the plots are shown as Figures 6 and 7, respectively. The value of β_4 was obtained as the slope of the best straight line that could be drawn through the points obtained by plotting X_3 vs. [A] (Figure 7).

The overall concentration stability constants obtained are:

$$\beta_1 = 4.8 \pm 0.4 \times 10^2 \ M^{-1}$$

$$\beta_2 = 1.0 \pm 0.1 \times 10^4 \ M^{-2}$$

$$\beta_3 = 1.5 \pm 0.2 \times 10^5 \ M^{-3}$$

$$\beta_4 = 2.0 \pm 1.6 \times 10^5 \ M^{-4}$$

The first three values represent reasonable indications of the overall stability constants. The final value, β_4, can be accepted only as an indication of the order of magnitude of the quantity in question. This is frequently the case in studies of this type. By the nature of the processes involved here, the accidental error must exhibit a cumulative characteristic which will be a maximum at the final number (β_4 in this case). The uncertainty reported for the values β_1 and β_2 should represent very nearly the maximum accidental error. The uncertainty associated with the value β_4 and to some extent β_3 is very possibly less than the maximum error. The situation arises partially from graphical inadequacies, but in far greater measure from the nature of the reaction system. The quantities on which β_3 and β_4 depend most are those which results from addition of relatively large amounts of ligand to the metal ion solutions. The metal ion - ligand interactions are at a maximum and so must be the disturbances experienced by the ionic

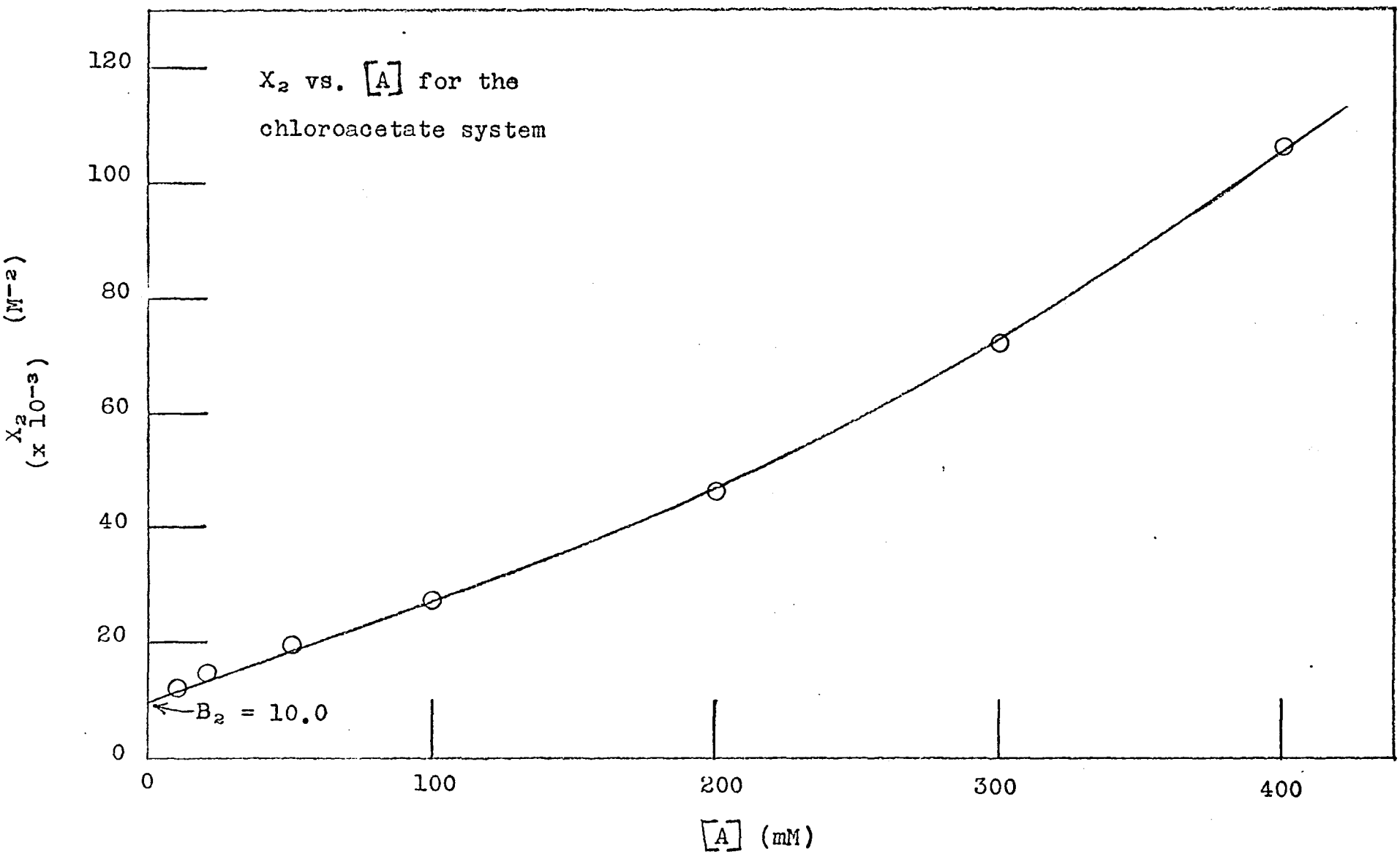
X_2 vs. [A] for the
chloroacetate system
120
100
80
60
40
20
0
X_2 ($\times 10^{-3}$) (M^{-2})
B_2 = 10.0
0
100
200
300
400
[A] (mM)

Fig. 6

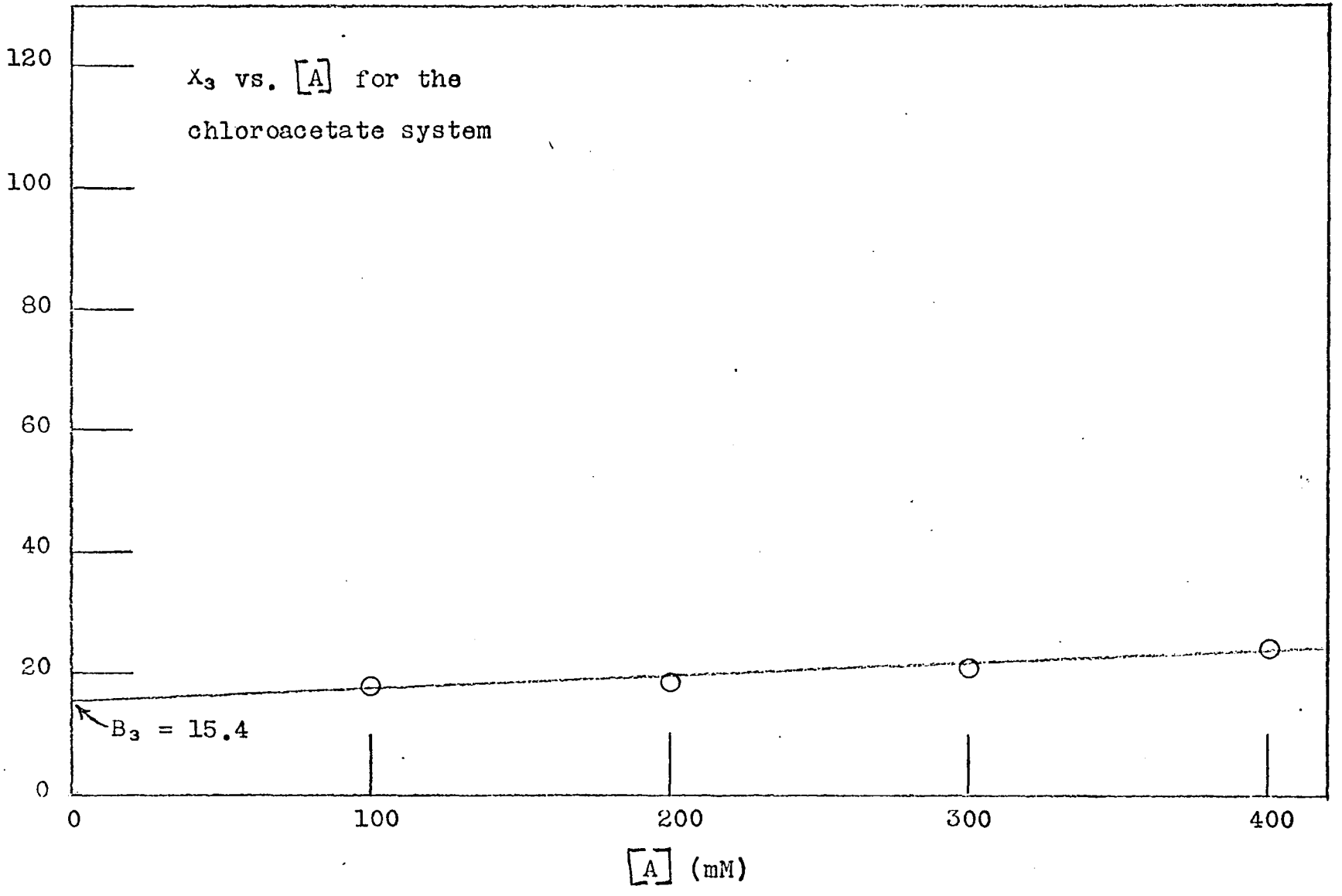
X_3 vs. [A] for the
chloroacetate system
120
100
80
60
40
20
0
X_3 (M^{-3})
($\times 10^{-4}$)
B_3 = 15.4
0
100
200
300
400
[A] (mM)

Fig. 7

medium. This could contribute in a very fundamental way to the uncertainty associated with the values of β_4 and β_3.

The stepwise concentration stability constants for the monochloroacetate system at 25°C are as follows:

$$K_1 = 480\ M^{-1}$$

$$K_2 = 21\ M^{-1}$$

$$K_3 = 15\ M^{-1}$$

$$K_4 = 1.3\ M^{-1}$$

The distribution of the metal ion in the various complexes as a function of [A] was calculated, and the results of this calculation are summarized in Table III. The f values indicate the fraction of the metal ion appearing in a particular complex or

$$f_n = \frac{[MA_n]}{C_M}$$

$$f_o = \frac{[M]}{C_M} \quad .$$

Recalling that

$$C_M = [M]X \ ,$$

it can be seen that

$$f_o = \frac{[M]}{C_M} = \frac{1}{X} \quad . \tag{26}$$

For the calculation of f_1, the system

$$M + A \rightleftarrows MA$$

TABLE III

DISTRIBUTION OF THE METAL ION IN THE VARIOUS COMPLEXES AS A FUNCTION OF THE FREE LIGAND CONCENTRATION FOR THE CHLOROACETATE SYSTEM

Free Ligand Conc., [A]	$f_o = \frac{[M]}{C_M}(100)$	$f_1 = \frac{[MA]}{C_M}(100)$	$f_2 = \frac{[MA_2]}{C_M}(100)$	$f_3 = \frac{[MA_3]}{C_M}(100)$	$f_4 = \frac{[MA_4]}{C_M}(100)$
mM	%	%	%	%	%
1.0	67.1	32.1	0.7	0.0	0.0
5.0	26.4	63.4	6.6	0.5	0.0
10.0	14.3	68.6	14.3	2.2	0.0
20.0	6.1	58.1	24.2	7.5	0.2
100	0.3	14.8	30.9	47.5	6.3
200	0.0	0.5	20.6	63.5	16.7
400	0.0	0.1	9.4	57.6	30.4

must be considered, and noting that

$$[MA] = \beta_1 [M][A],$$

it can be seen that

$$f_1 = \frac{[MA]}{C_M} = \frac{B_1 [M][A]}{C_M} = \frac{\beta_1 [A]}{X} \quad . \qquad (27)$$

For any value of f_n

$$f_n = \frac{\beta_n [A]^n}{X} \quad . \qquad (28)$$

The values in Table III were calculated on the basis of equation (28). At very low ligand concentrations there are relatively high percentages of $In^{3+}_{(aq)}$ and $In(OAcCl)^{2+}$, whereas at high ligand concentrations $In(OAcCl)_3$ seems to be the most abundant entity. There are appreciable quantities of $In(OAcCl)_4^{1-}$ at the highest ligand concentration. Also the trend of the f_n values at the highest ligand concentrations apparently demonstrates that the formation of $In(OAcCl)_5^{2-}$ and higher complexes is not an extremely favorable process. It must be noted again, however, that this latter conclusion is based on that segment of the experimental data which bears the greatest uncertainty.

2-Chloropropionate system. The e.m.f. and related data for the 2-chloropropionate system are presented in Table IV. The titration procedure used in the 2-chloropropionate system was essentially the same as that employed in the chloroacetate system. The fundamental differences were the inclusion of one more ligand aliquot at C_A = 25.97 mM and the introduction of a 3:1 acid-to-anion buffer concentration ratio, in place of the 4:1 ratio used in the chloroacetate system. The change in the buffer ratio was adopted for several reasons. In the actual

TABLE IV

DATA SUMMARY FOR THE 2-CHLOROPROPIONATE SYSTEM

($C_S = 0.162\ C_M$)

Total Metal Ion Conc., C_M mM	Total Ligand Conc., C_A mM	E_o* mV	E mV	E_A (E_o -E) mV	Free Ligand Conc., [A] mM	$\frac{\bar{n}}{[A]}$ 1/M
	Buffer: 2-Chloropropionic acid/2-Chloropropionate = 3/1					
9.87	13.16	51.87	32.65	19.22	7.28	137.6
9.74	25.97	49.05	34.40	14.64	16.23	84.78
9.62	38.46	48.10	36.18	11.93	26.06	62.74
9.38	62.50	47.66	38.82	8.84	46.57	43.10
9.15	85.36	47.80	40.73	7.07	67.31	33.56
8.82	117.6	48.31	42.72	5.58	97.30	26.40
8.33	166.7	49.42	45.19	4.23	144.1	20.58
7.89	210.5	50.59	47.08	3.51	186.4	17.69
7.50	250.0	51.72	48.76	2.96	225.4	15.60
7.14	285.7	52.92	50.26	2.66	260.2	14.62
6.82	318.2	53.98	51.59	2.39	292.4	13.73
6.52	347.8	55.03	52.82	2.20	321.7	13.16
6.00	400.0	56.92	55.04	1.87	374.2	12.10

continued-

*E_o = e.m.f. when $C_M = 0$

TABLE IV-2

Total Metal Ion Conc., C_M / mM	Total Ligand Conc., C_A / mM	E_o* / mV	E / mV	E_A (E_o -E) / mV	Free Ligand Conc., [A] / mM	$\bar{n}$ / [A] / 1/M
19.74	13.16	51.87	19.18	32.68	4.10	189.5
19.48	25.97	49.05	21.48	27.58	9.60	117.0
19.23	38.46	48.10	24.55	23.56	16.41	84.34
18.75	62.50	47.66	29.44	18.21	32.27	55.44
18.29	85.36	47.80	32.93	14.87	49.70	42.07
17.65	117.6	48.31	36.60	11.72	76.69	31.66
16.67	166.7	49.42	40.56	8.86	120.5	23.71
15.80	210.5	50.59	43.42	7.18	161.7	19.54
15.00	250.0	51.72	45.66	6.06	200.0	16.98
14.28	285.7	52.92	47.53	5.39	234.2	15.65
13.64	318.2	53.98	49.16	4.82	266.2	14.52
13.04	347.8	55.03	50.64	4.40	295.5	13.75
12.00	400.0	56.92	53.17	3.74	348.2	12.54

*E_o = e.m.f. when C_M = 0

continued-

TABLE IV-3

Total Metal Ion Conc., C_M mM	Total Ligand Conc., C_A mM	E_o* mV	E mV	E_A (E_o -E) mV	Free Ligand Conc., [A] mM	$\frac{\bar{n}}{[A]}$ 1/M
39.47	13.16	51.87	3.60	48.26	1.99	282.4
38.96	25.97	49.05	4.61	44.44	4.69	173.3
38.46	38.46	48.10	7.00	41.10	8.00	128.2
37.50	62.50	47.66	12.94	34.72	16.36	85.02
36.58	85.36	47.80	18.32	29.48	28.01	59.76
35.29	117.6	48.31	24.59	23.72	48.08	42.14
33.33	166.7	49.42	31.50	17.92	84.86	29.11
31.58	210.5	50.59	36.16	14.44	122.2	22.82
30.00	250.0	51.72	39.64	12.08	158.6	19.08
28.57	285.7	52.92	42.42	10.50	192.4	16.83
27.27	318.2	53.98	44.68	9.30	224.1	15.25
26.09	347.8	55.03	46.63	8.40	253.3	14.15
24.00	400.0	56.92	49.78	7.13	305.5	12.75

*E_o = e.m.f. when C_M = 0

continued-

TABLE IV-4

Total Metal Ion Conc., C_M / mM	Total Ligand Conc., C_A / mM	E_o* / mV	E / mV	E_A (E_o -E) / mV	Free Ligand Conc., [A] / mM	$\bar{n}$/[A] / 1/M
	Buffer: 2-Chloropropionic acid/2-Chloropropionate = 1/1					
19.74	13.16	78.75	32.76	45.99	2.11	322.7
19.23	38.46	76.25	46.23	30.02	12.54	108.3
18.75	62.50	75.90	54.28	21.62	28.10	64.13
18.29	85.36	75.84	58.92	16.92	45.75	46.21
17.65	117.6	76.02	63.11	12.91	73.10	33.61
16.67	166.7	76.39	67.06	9.33	118.2	23.99
15.80	210.5	76.78	69.42	7.36	160.5	19.23
15.00	250.0	77.20	71.06	6.14	199.4	16.52
14.28	285.7	77.65	72.28	5.37	234.3	15.03
13.64	318.2	77.97	73.33	4.64	268.2	13.38
13.04	347.8	78.31	74.14	4.17	298.2	12.50
12.00	400.0	78.99	75.50	3.49	351.6	11.26

*E_o = e.m.f. when C_M = 0

experimental sequence the 3-chloropropionate system was completed prior to the 2-chloropropionate system. In order to insure the complete solubility of 3-chloropropionic acid, it was deemed advisable to drop the acid concentration to 3 M. Also in the case of both the 2- and 3-chloropropionate systems, lowering the concentration of the acid reduced the rate of the acid hydrolysis process.

The plots of $\frac{\bar{n}}{[\overline{A}]}$ vs. [A] are shown as Figures 8 and 9. There was no evidence of polynuclear complex formation or any appreciable metal ion hydrolysis. The fact that there are no apparent anomalies experienced in the trends of the e.m.f. values, and therefore in the [A] and $\bar{n}$ quantities, seems to offer further indication that no disturbing chemical situation was occurring in the ligand solutions (see Appendix I).

The data used to calculate the β_n values are shown in Table V. The $\bar{n}$ values again were determined graphically and suggested the possibility of obtaining five β_n values from the available data. The X values were determined by the use of equation (25). The expressions for the X_n in the 2-chloropropionate system are as follows:

$$X_1 = \frac{(X-1)}{[A]} = \beta_1 + \beta_2[A] + \beta_3[A]^2 + \beta_4[A]^3 + \beta_5[A]^4$$

$$X_2 = \frac{(X_1-\beta_1)}{[A]} = \beta_2 + \beta_3[A] + \beta_4[A]^2 + \beta_5[A]^3$$

$$X_3 = \frac{(X_2-\beta_2)}{[A]} = \beta_3 + \beta_4[A] + \beta_5[A]^2$$

$$X_4 = \frac{(X_3-\beta_3)}{[A]} = \beta_4 + \beta_5[A]$$

Plots of X_1, X_2, X_3 and X_4, as a function of [A] extrapolated to [A] = 0, gave values of β_1, β_2, β_3 and β_4. These plots are included as Figures 10 through 13. The value of β_5 was obtained from the slope of the best straight line in the plot

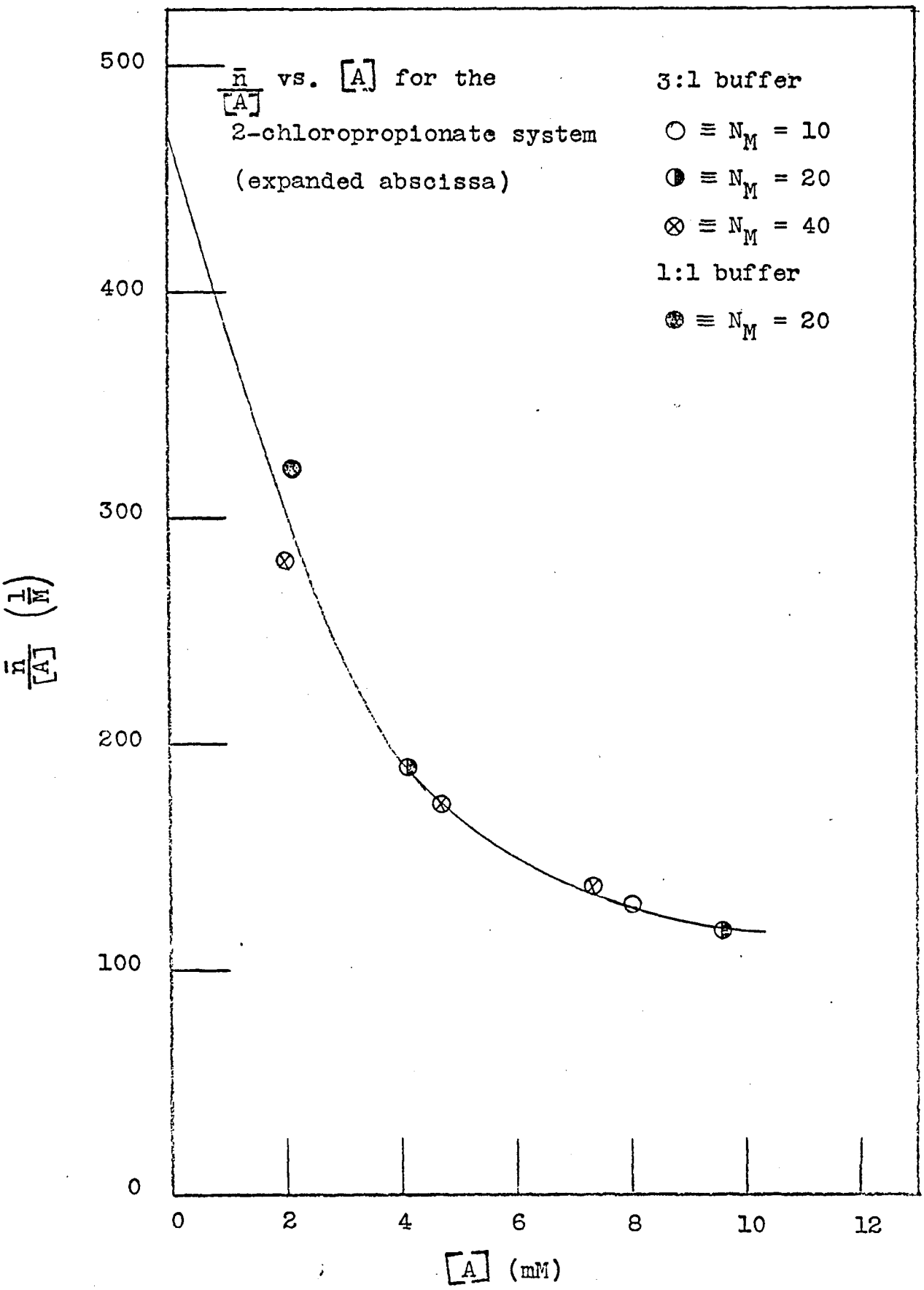
$\frac{\bar{n}}{[A]}$ vs. [A] for the
2-chloropropionate system
(expanded abscissa)
3:1 buffer
○ ≡ N_M = 10
◑ ≡ N_M = 20
⊗ ≡ N_M = 40
1:1 buffer
◍ ≡ N_M = 20
$\frac{\bar{n}}{[A]}$ $\left(\frac{1}{M}\right)$
500
400
300
200
100
0
0
2
4
6
8
10
12
[A] (mM)

Fig. 8

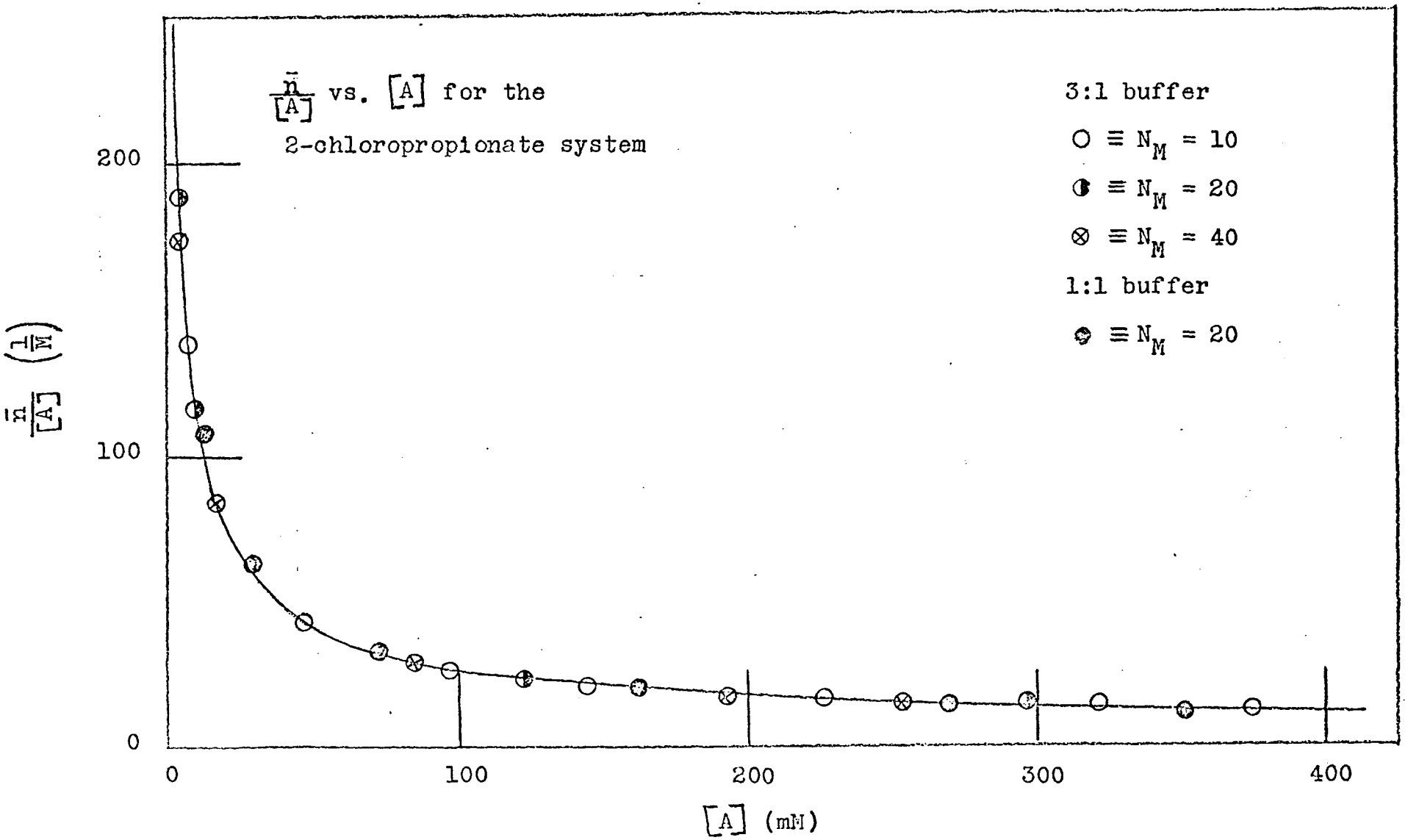
$\frac{\bar{n}}{[A]}$ vs. [A] for the
2-chloropropionate system
3:1 buffer
○ ≡ N_M = 10
◑ ≡ N_M = 20
⊗ ≡ N_M = 40
1:1 buffer
◒ ≡ N_M = 20
$\frac{\bar{n}}{[A]}$ $\left(\frac{l}{M}\right)$
200
100
0
0
100
200
300
400
[A] (mM)

Fig. 9

TABLE V

DATA FOR THE DETERMINATION OF THE OVERALL STABILITY CONSTANTS FOR THE 2-CHLOROPROPIONATE SYSTEM

Free Ligand Conc., [A] mM	Ligand Number, $\bar{n}$	$\int_0^{[A]_j} \frac{\bar{n}}{[A]} d[A]$	X	X_1 M^{-1}	$X_2 \cdot 10^{-3}$ M^{-2}	$X_3 \cdot 10^{-4}$ M^{-3}	$X_4 \cdot 10^{-5}$ M^{-4}
1.0	0.381	0.4283	1.53	530	-	-	-
5.0	0.825	1.431	4.18	636	-	-	-
10.0	1.15	2.101	8.17	717	19.9	-	-
20.0	1.55	3.005	20.2	960	22.1	20	-
50.0	2.05	4.665	106	2100	31.6	27	-
100	2.60	6.254	520	5190	46.7	28.6	9.4
200	3.26	8.315	4080	$2.04 \cdot 10^4$	99.4	40.6	10.7
300	3.84	9.730	$1.68 \cdot 10^4$	$5.60 \cdot 10^4$	185	55.6	12.1
400	4.40	10.94	$5.63 \cdot 10^4$	$1.41 \cdot 10^5$	351	83.2	16.0

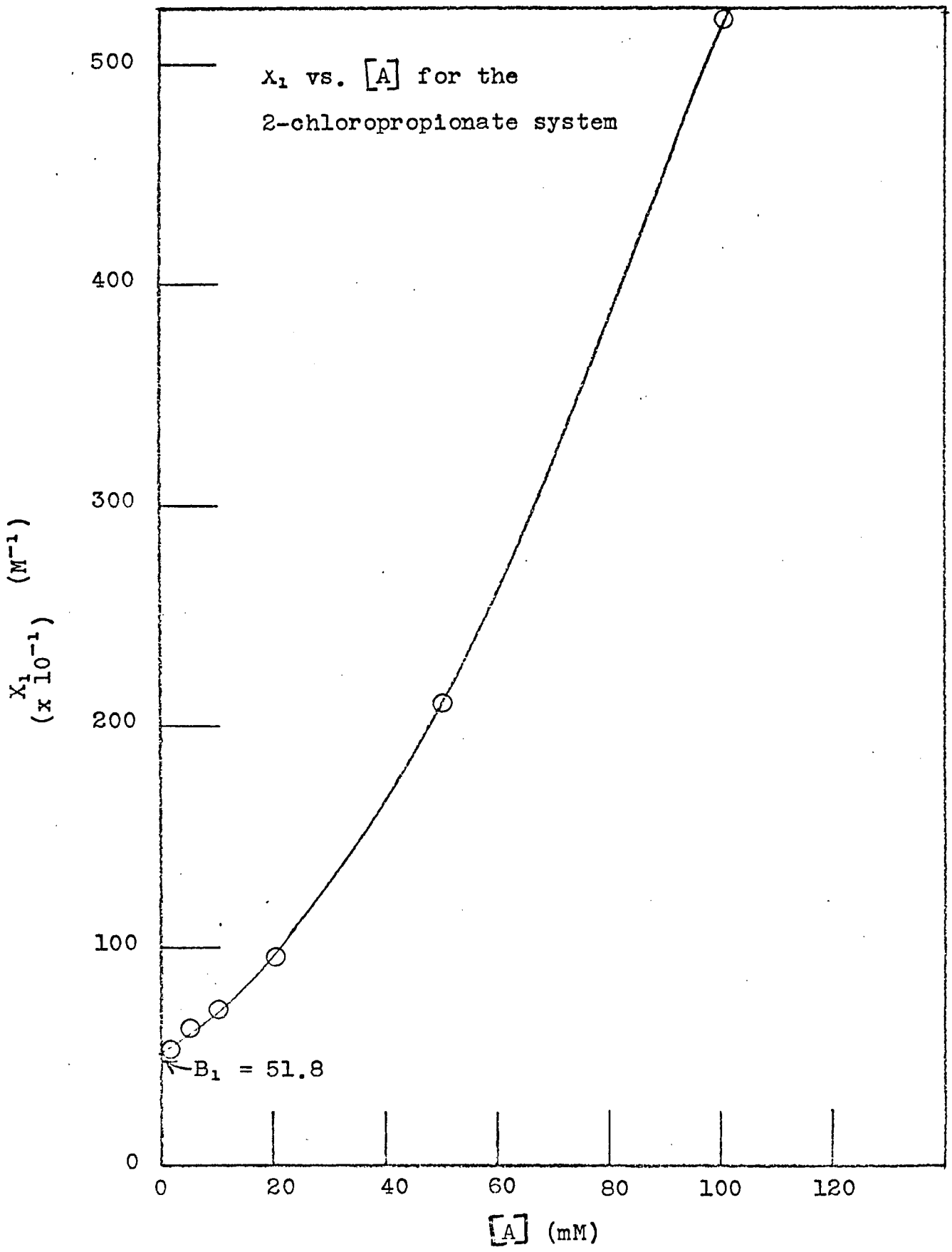
X_1 vs. [A] for the
2-chloropropionate system
500
400
300
200
100
0
X_1 ($\times 10^{-1}$) (M^{-1})
B_1 = 51.8
0
20
40
60
80
100
120
[A] (mM)

Fig. 10

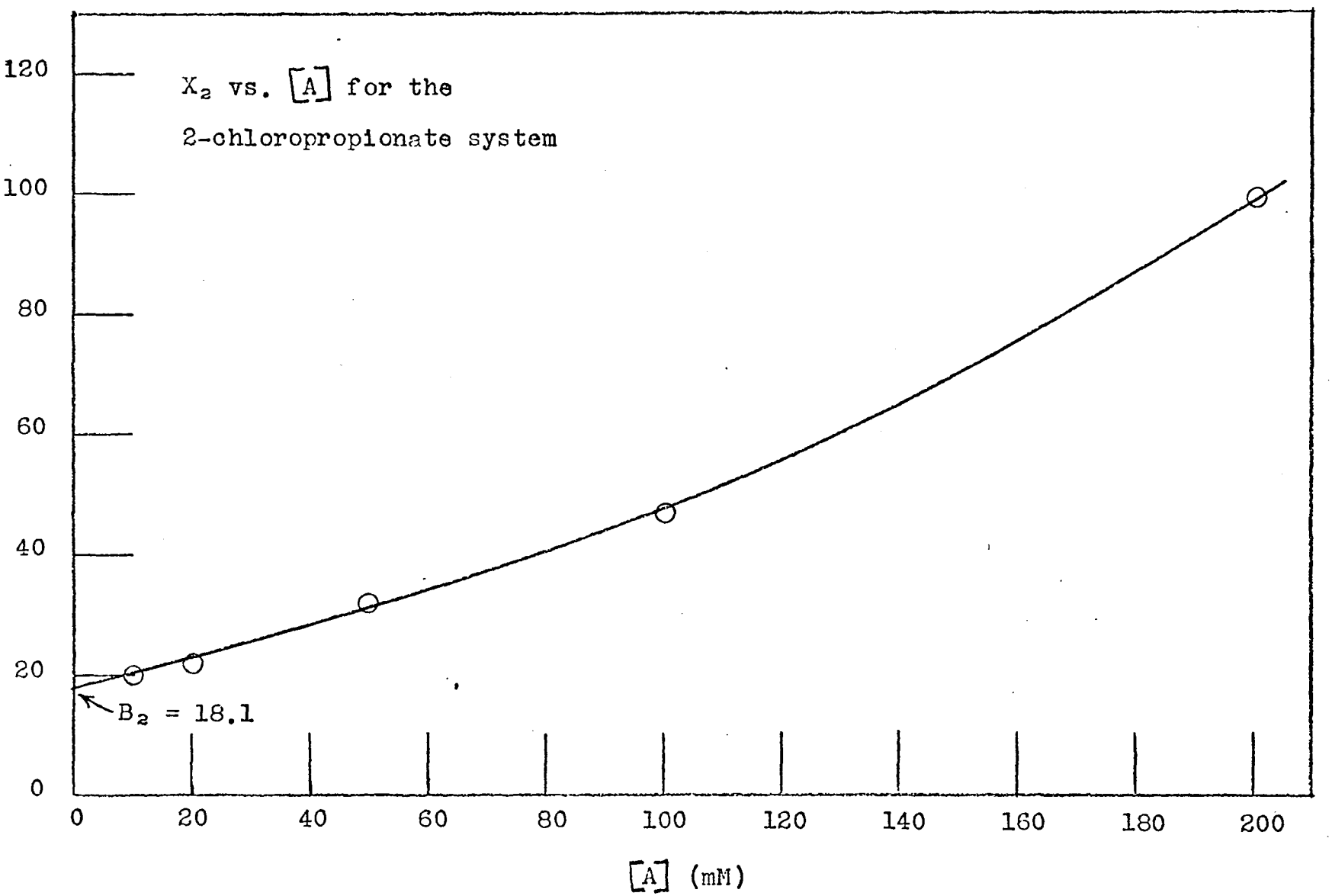
X_2 vs. [A] for the
2-chloropropionate system
B_2 = 18.1
X_2 ($\times 10^{-3}$) (M^{-2})
[A] (mM)
0
20
40
60
80
100
120
140
160
180
200

Fig. 11

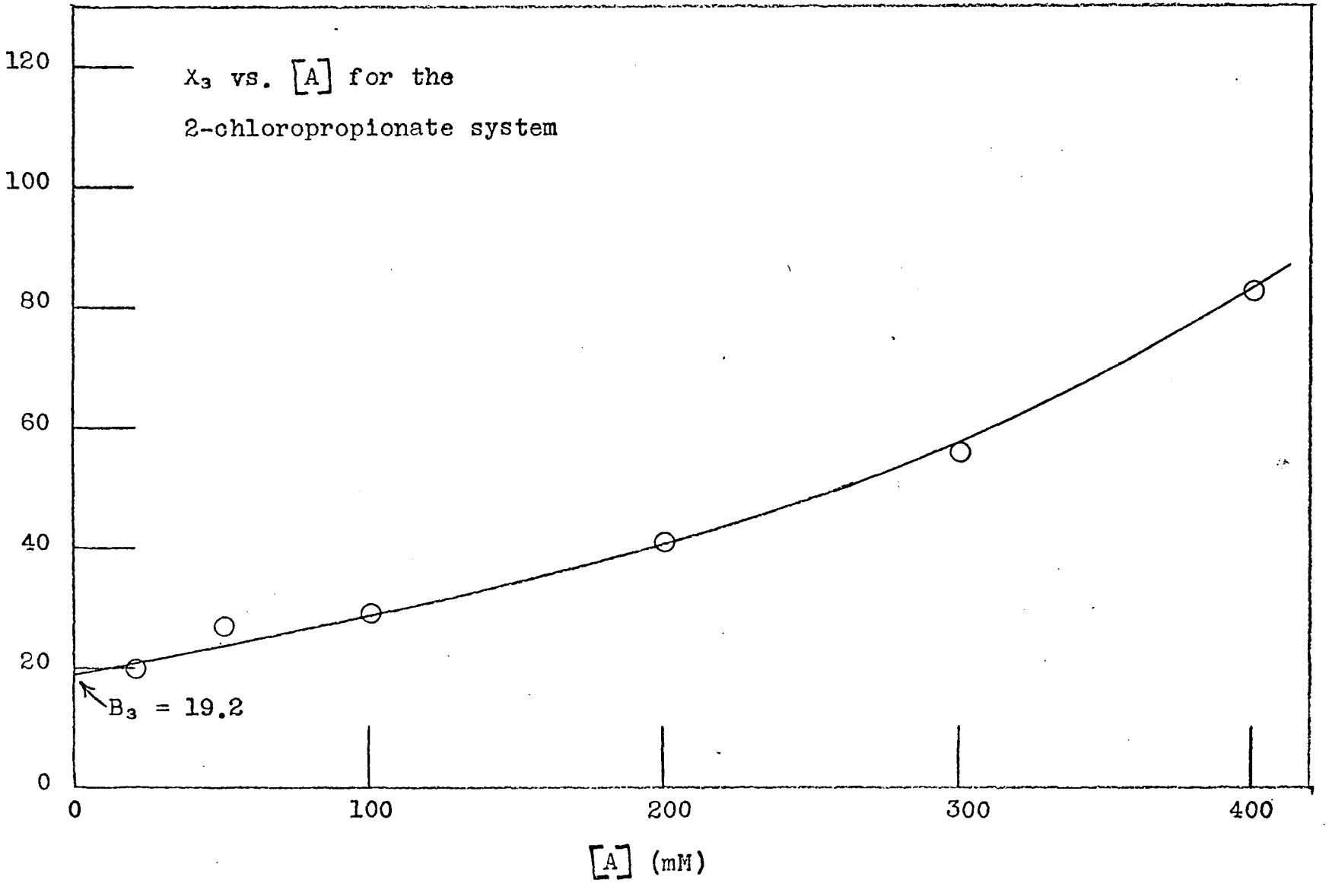
X_3 vs. [A] for the
2-chloropropionate system
120
100
80
60
40
20
0
X_3 ($\times 10^{-4}$) (M^{-3})
B_3 = 19.2
0
100
200
300
400
[A] (mM)

Fig. 12

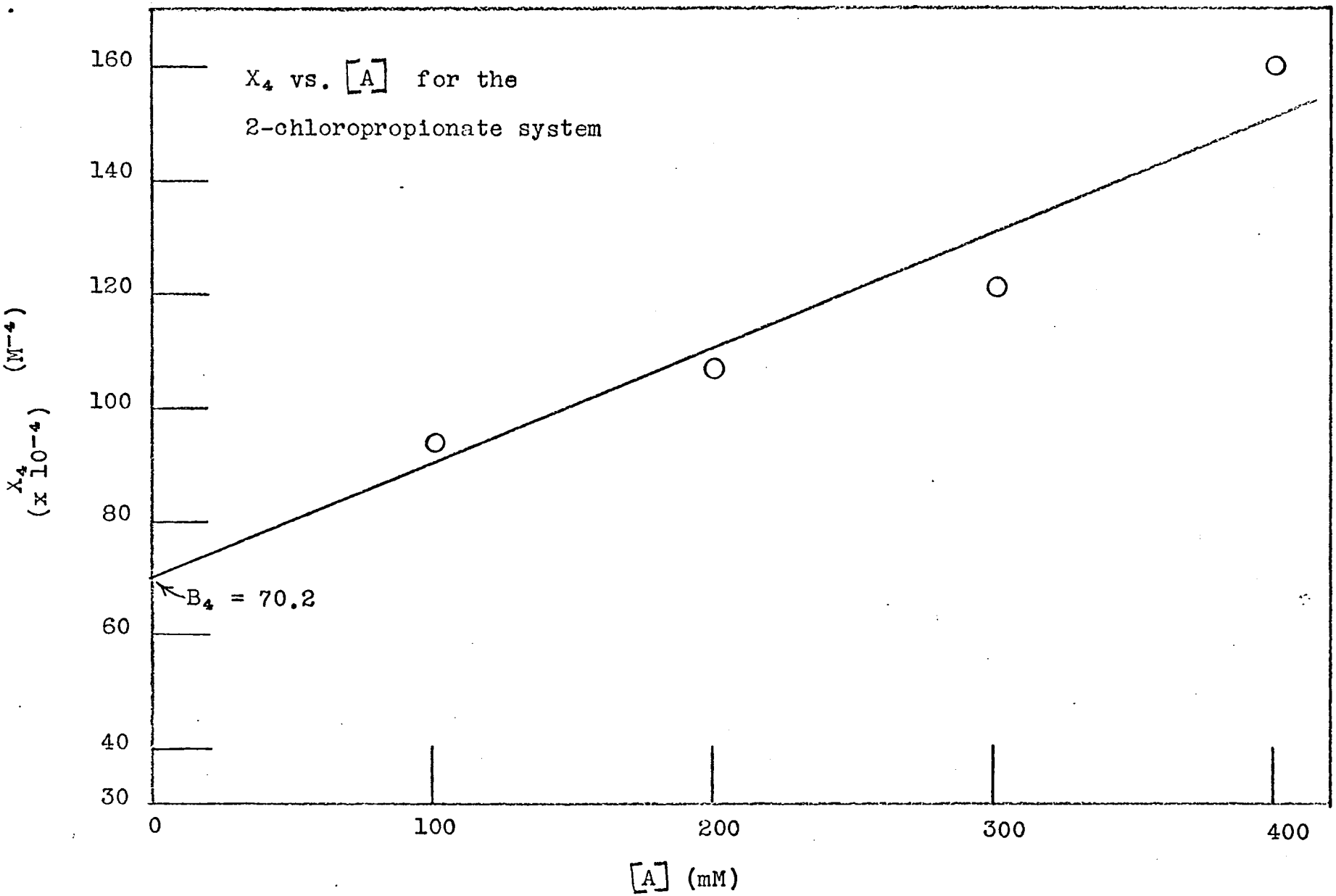
X_4 vs. [A] for the
2-chloropropionate system
160
140
120
100
80
60
40
30
X_4 (M^{-4})
($\times 10^{-4}$)
B_4 = 70.2
0
100
200
300
400
[A] (mM)

Fig. 13

of X_4 as a function of [A].

The β_n values obtained were as follows:

$$\beta_1 = 5.2 \pm 0.1 \times 10^2 \quad M^{-1}$$

$$\beta_2 = 1.8 \pm 0.15 \times 10^4 \quad M^{-2}$$

$$\beta_3 = 1.9 \pm 0.3 \times 10^5 \quad M^{-3}$$

$$\beta_4 = 7.0 \pm 1.5 \times 10^5 \quad M^{-4}$$

$$\beta_5 = 2.0 \pm 1.1 \times 10^6 \quad M^{-5}$$

Again it should be emphasized, that although the first three constants may be considered to be reasonably dependable, the last two values, and in particular β_5, might best be accepted as indicating order of magnitude effects. It is of interest to note that the β_n values for the 2-chloropropionate system exhibited order of magnitude agreement with the β_n values of the chloroacetate system.

The K_n values, as defined in equation (23), were as follows:

$$K_1 = 520 \ M^{-1}$$

$$K_2 = 35 \ M^{-1}$$

$$K_3 = 10 \ M^{-1}$$

$$K_4 = 3.7 \ M^{-1}$$

$$K_5 = 2.8 \ M^{-1}$$

The distribution of the metal ion in the different complex species as a function of [A] for the 2-chloropropionate system is shown in Table VI. These values were calculated

TABLE VI

DISTRIBUTION OF THE METAL ION IN THE VARIOUS COMPLEXES AS A FUNCTION OF THE FREE LIGAND CONCENTRATION FOR THE 2-CHLOROPROPIONATE SYSTEM

Free Ligand Conc., [A]	$f_o = \frac{[M]}{C_M}(100)$	$f_1 = \frac{[MA]}{C_M}(100)$	$f_2 = \frac{[MA_2]}{C_M}(100)$	$f_3 = \frac{[MA_3]}{C_M}(100)$	$f_4 = \frac{[MA_4]}{C_M}(100)$	$f_5 = \frac{[MA_5]}{C_M}(100)$
mM	%	%	%	%	%	%
1.0	65.4	33.8	1.2	0.0	0.0	0.0
5.0	23.9	62.0	10.8	0.6	0.0	0.0
10.0	12.2	63.4	22.2	2.4	0.1	0.0
20.0	5.0	51.3	35.8	7.6	0.6	0.0
100	0.2	10.0	34.8	36.9	13.5	3.9
200	0.0	2.5	17.7	37.6	27.5	15.8
400	0.0	0.4	5.1	21.8	31.9	36.7

using equation (28). The nature of this distribution is generally similar to that for the chloroacetate system. The most striking difference occurs at the highest ligand concentration. It would appear that the species $In(PrCl)_5^{2-}$ is present in significant quantities. This, in turn, probably indicates that the maximum coordination number for the indium-2-chloropropionate system tends toward six. It was not thought justifiable on the basis of the experimental data, most particularly the maximum value of $\bar{n}$, to calculate a sixth β and K value.

3-Chloropropionate system. A data summary table for the 3-chloropropionate ligand system is shown as Table VII.

The plots of $\frac{\bar{n}}{[A]}$ vs. [A] for the 3-chloropropionate system appear as Figures 14 and 15. Critical examination of these curves revealed no evidence of polynuclear complex formation or metal ion hydrolysis. This system, of the three studied, is the one in which metal ion hydrolysis might most possibly occur. The acid constant of 3-chloropropionic acid is about one order of magnitude smaller than the other two acids. However, as was indicated above, there was no experimental evidence that hydrolysis effects did occur. In this system, as in the other two reported, there was no evidence of spurious trends or unaccountable discontinuities in the observed e.m.f.'s. This suggested once again the absence of disturbing chemical effects in the ligand solutions.

The results of the graphical integration and the related quantities for the 3-chloropropionate system are shown in Table VIII. The $\bar{n}$ values, also listed in Table VIII, indicated that five stability constants could be extracted from this data with considerable confidence. The values X_1 through X_4 were determined using the same expressions as those used in the 2-chloropropionate system. The plots of the X_n vs. [A]

TABLE VII

DATA SUMMARY FOR THE 3-CHLOROPROPIONATE SYSTEM

($C_S = 0.162\ C_M$)

Total Metal Ion Conc., C_M mM	Total Ligand Conc., C_A mM	E_o* mV	E mV	E_A (E_o -E) mV	Free Ligand Conc., [A] mM	$\bar{n}/[A]$ 1/M
	Buffer: 3-Chloropropionic acid/3-Chloropropionate = 3/1					
9.87	13.16	116.92	67.68	49.24	1.98	563.6
9.74	25.97	116.96	87.20	29.76	8.34	205.9
9.62	38.46	117.08	95.03	22.04	16.59	130.4
9.38	62.50	117.42	103.22	14.20	36.35	73.29
9.15	85.36	117.89	107.21	10.68	56.76	52.82
8.82	117.6	118.51	110.54	7.96	86.80	38.71
8.33	166.7	119.50	113.86	5.64	134.3	27.97
7.89	210.5	120.46	116.02	4.44	177.6	22.72
7.50	250.0	121.44	117.68	3.76	216.5	20.00
7.14	285.7	122.28	119.09	3.19	252.9	17.63
6.82	318.2	123.14	120.32	2.82	285.6	16.26
6.52	347.8	123.88	121.36	2.53	315.6	15.22
6.00	400.0	125.30	123.18	2.13	368.7	13.79

continued-

*E_o = e.m.f. when $C_M = 0$

TABLE VII-2

Total Metal Ion Conc., C_M / mM	Total Ligand Conc., C_A / mM	E_o^* / mV	E / mV	E_A (E_o -E) / mV	Free Ligand Conc., [A] / mM	$\frac{\bar{n}}{[A]}$ / 1/M
19.74	13.16	116.92	39.64	77.27	0.65	1058.5
19.48	25.97	116.96	52.84	64.12	2.18	545.9
19.23	38.46	117.08	67.50	49.57	5.71	283.0
18.75	62.50	117.42	84.55	32.88	17.67	128.4
18.29	85.36	117.89	93.56	24.33	33.54	80.50
17.65	117.6	118.51	100.90	17.62	59.78	52.46
16.67	166.7	119.50	107.28	12.22	104.3	34.52
15.80	210.5	120.46	111.08	9.38	146.8	26.47
15.00	250.0	121.44	113.65	7.79	185.4	22.44
14.28	285.7	122.28	115.60	6.68	221.0	19.84
13.64	318.2	123.14	117.26	5.88	253.8	18.03
13.04	347.8	123.88	118.69	5.20	284.7	16.48
12.00	400.0	125.30	120.96	4.34	338.6	14.68

*E_o = e.m.f. when C_M = 0

continued-

TABLE VII-3

Total Metal Ion Conc., C_M mM	Total Ligand Conc., C_A mM	E_o^* mV	E mV	E_A (E_o -E) mV	Free Ligand Conc., [A] mM	$\frac{\bar{n}}{[A]}$ 1/M
39.47	13.16	116.92	14.62	102.29	0.22	2059.1
38.96	25.97	116.96	22.69	94.27	0.65	1076.9
38.46	38.46	117.08	30.48	86.59	1.33	723.3
37.50	62.50	117.42	48.39	69.04	4.34	338.7
36.58	85.36	117.89	63.76	54.13	10.59	182.0
35.29	117.6	118.51	79.52	38.99	26.21	93.59
33.33	166.7	119.50	93.57	25.92	61.50	48.94
31.58	210.5	120.46	100.99	19.47	99.54	33.80
30.00	250.0	121.44	105.66	15.78	136.3	26.70
28.57	285.7	122.28	109.01	13.26	171.6	22.39
27.27	318.2	123.14	111.56	11.58	203.8	19.83
26.09	347.8	123.88	113.66	10.23	234.6	17.84
24.00	400.0	125.30	116.81	8.50	288.4	15.59

*E_o = e.m.f. when C_M = 0

continued-

TABLE VII-4

Total Metal Ion Conc., C_M / mM	Total Ligand Conc., C_A / mM	E_o* / mV	E / mV	E_A (E_o -E) / mV	Free Ligand Conc., [A] / mM	$\frac{\bar{n}}{[A]}$ / 1/M
	Buffer: 3-Chloropropionic acid/3-Chloropropionate = 1/1					
19.74	13.16	143.34	50.22	93.12	0.36	1750.0
19.48	25.97	143.36	70.10	73.26	1.62	713.0
19.23	38.46	143.40	86.24	57.16	4.44	370.0
18.75	62.50	143.50	107.65	35.85	16.21	143.3
18.29	85.36	143.69	118.22	25.47	32.78	83.10
17.65	117.6	143.95	126.17	17.78	60.27	51.35
16.67	166.7	144.38	132.39	11.99	106.2	32.71
15.80	210.5	144.83	135.63	9.20	148.9	25.14
15.00	250.0	145.09	137.72	7.37	189.5	20.46
14.28	285.7	145.47	139.21	6.26	225.8	17.89
13.64	318.2	145.84	140.37	5.47	259.0	16.15
13.04	347.8	-	141.32	-	-	-
12.00	400.0	146.64	142.78	3.86	345.9	12.58

*E_o = e.m.f. when C_M = 0

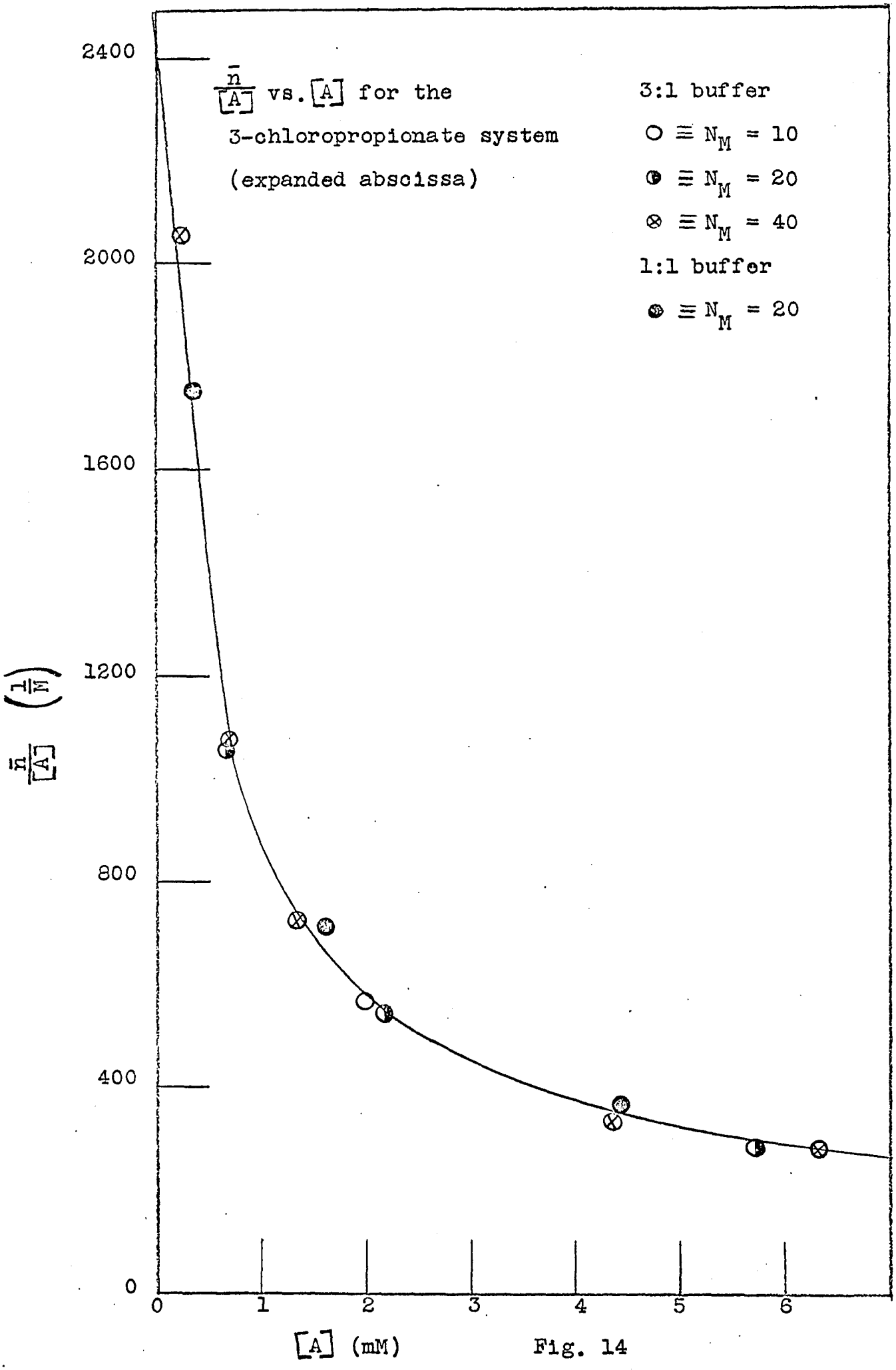
$\frac{\bar{n}}{[A]}$ vs. [A] for the
3-chloropropionate system
(expanded abscissa)
3:1 buffer
○ ≡ N_M = 10
◔ ≡ N_M = 20
⊗ ≡ N_M = 40
1:1 buffer
◍ ≡ N_M = 20
2400
2000
1600
1200
800
400
0
$\left(\frac{1}{M}\right)$
$\frac{\bar{n}}{[A]}$
0
1
2
3
4
5
6
[A] (mM)

Fig. 14

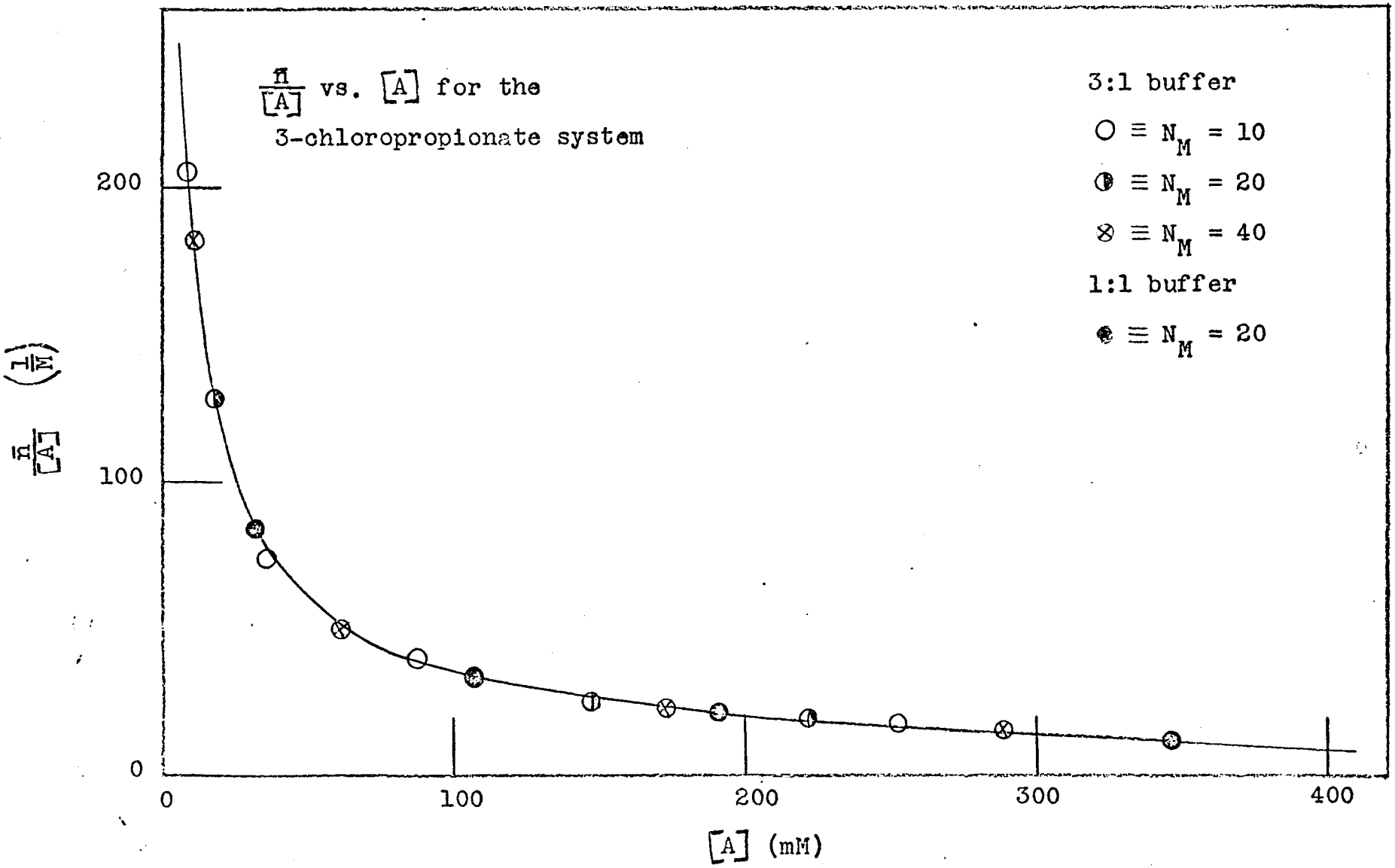
$\frac{\bar{n}}{[A]}$ vs. [A] for the
3-chloropropionate system
3:1 buffer
○ ≡ N_M = 10
◑ ≡ N_M = 20
⊗ ≡ N_M = 40
1:1 buffer
◉ ≡ N_M = 20
$\frac{\bar{n}}{[A]}$ $\left(\frac{1}{M}\right)$
200
100
0
0
100
200
300
400
[A] (mM)

Fig. 15

TABLE VIII

DATA FOR THE DETERMINATION OF THE OVERALL STABILITY CONSTANTS FOR THE 3-CHLOROPROPIONATE SYSTEM

Free Ligand Conc., [A] mM	Ligand Number, $\bar{n}$	$\int_0^{[A]_j} \frac{\bar{n}}{[A]} d[A]$	X	X_1 M^{-1}	$X_2 \cdot 10^{-5}$ M^{-2}	$X_3 \cdot 10^{-6}$ M^{-3}	$X_4 \cdot 10^{-7}$ M^{-4}	$X_5 \cdot 10^{-7}$ M^{-5}
1.0	0.847	1.496	4.46	3,460	-	-	-	-
5.0	1.62	3.447	31.4	6,080	6.36	-	-	-
10.0	1.85	4.691	109	$10.8 \cdot 10^3$	7.90	-	-	-
20.0	2.35	6.112	451	$22.5 \cdot 10^3$	9.80	21.5	-	-
50.0	2.96	8.580	5320	$10.6 \cdot 10^4$	20.6	30.2	-	-
100	3.28	10.67	$4.30 \cdot 10^4$	$4.30 \cdot 10^5$	42.7	37.2	21.2	(25)
200	3.98	13.21	$5.44 \cdot 10^5$	$2.72 \cdot 10^6$	136	65.2	24.6	(30)
300	4.50	14.92	$3.01 \cdot 10^6$	$1.00 \cdot 10^7$	333	109	31.0	(41)
400	4.96	16.28	$1.17 \cdot 10^7$	$2.92 \cdot 10^7$	730	181	41.2	(56)

are shown as Figures 16 through 19. The β_n values were determined in exactly the same manner as that described for the 2-chloropropionate system and were as follows:

$$\beta_1 = 2.9 \pm 0.4 \times 10^3 \quad M^{-1}$$

$$\beta_2 = 5.5 \pm 0.9 \times 10^5 \quad M^{-2}$$

$$\beta_3 = 1.6 \pm 0.4 \times 10^7 \quad M^{-3}$$

$$\beta_4 = 1.4 \pm 0.6 \times 10^8 \quad M^{-4}$$

$$\beta_5 = 6.4 \pm 4.5 \times 10^8 \quad M^{-5}$$

The dependability of these numbers must be evaluated within the framework of previous discussion.

The stepwise stability constants for the 3-chloropropionate system were determined to be:

$$K_1 = 2.9 \times 10^3$$

$$K_2 = 190$$

$$K_3 = 29$$

$$K_4 = 8.7$$

$$K_5 = 4.6$$

Table IX shows the distribution of the central ion in the various complexes as a function of [A]. It is of interest to examine that portion of the table which represents the highest concentrations of ligand. The species $In(PrCl)_5^{2-}$ is of great significance at these concentrations. The inference may be drawn here, as in the case of the

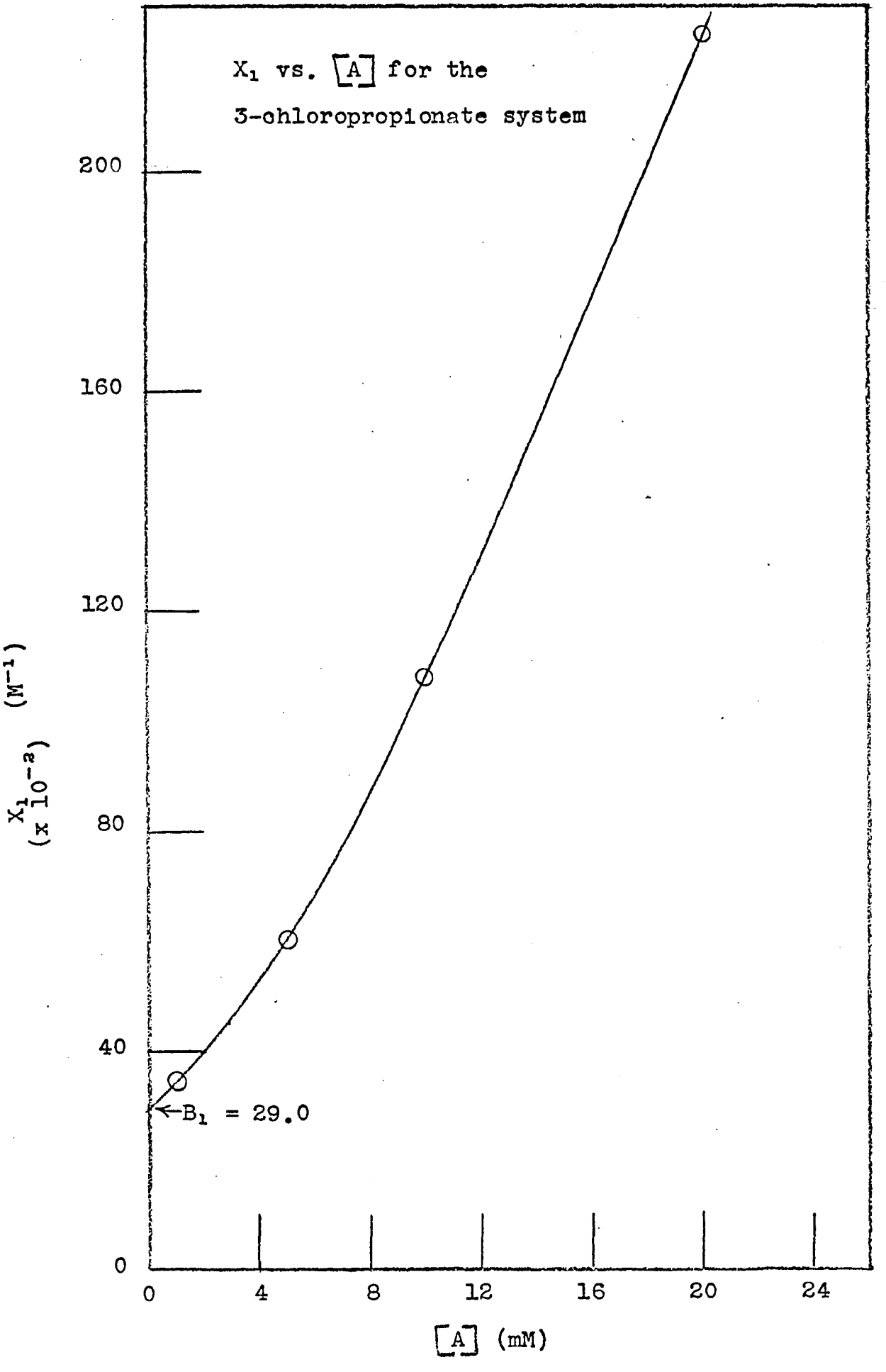
X_1 vs. [A] for the
3-chloropropionate system
200
160
120
80
40
0
X_1 ($\times 10^{-2}$) (M^{-1})
$\leftarrow B_1$ = 29.0
0
4
8
12
16
20
24
[A] (mM)

Fig. 16

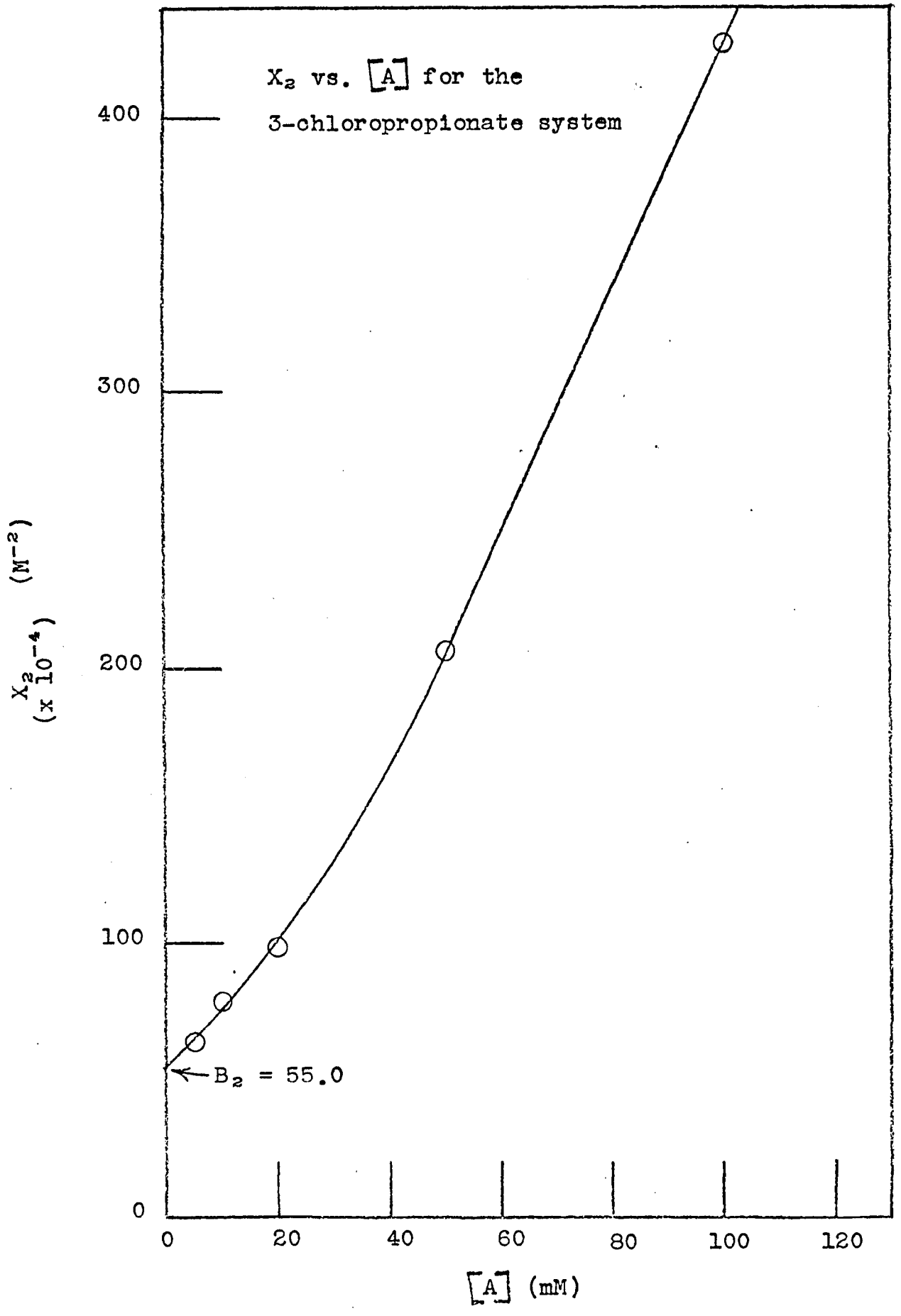
X_2 vs. [A] for the
3-chloropropionate system
400
300
200
100
0
X_2 ($\times 10^{-4}$) (M^{-2})
B_2 = 55.0
0
20
40
60
80
100
120
[A] (mM)

Fig. 17

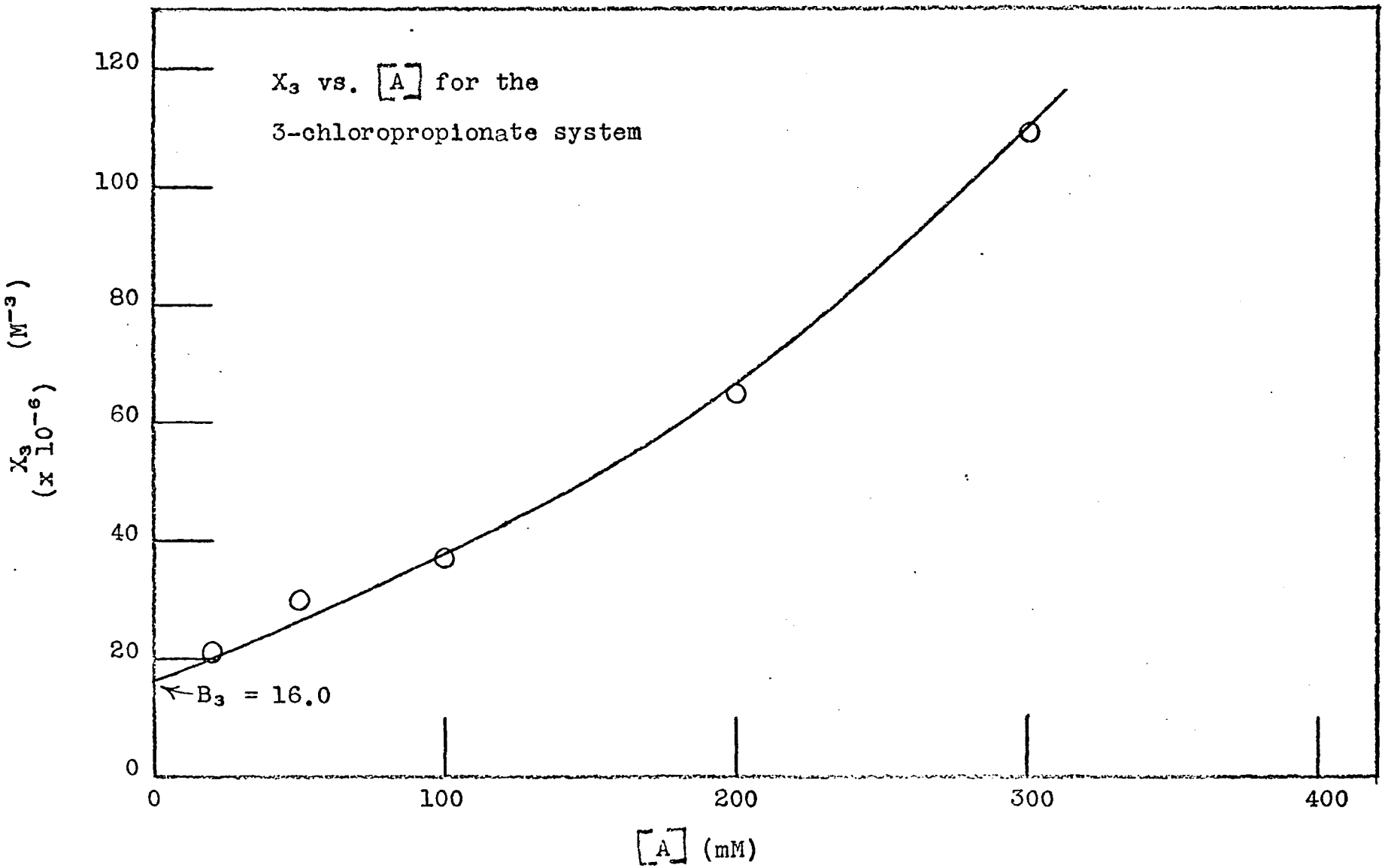
X_3 vs. [A] for the
3-chloropropionate system
120
100
80
60
40
20
0
X_3 ($\times 10^{-6}$) (M^{-3})
B_3 = 16.0
0
100
200
300
400
[A] (mM)

Fig. 18

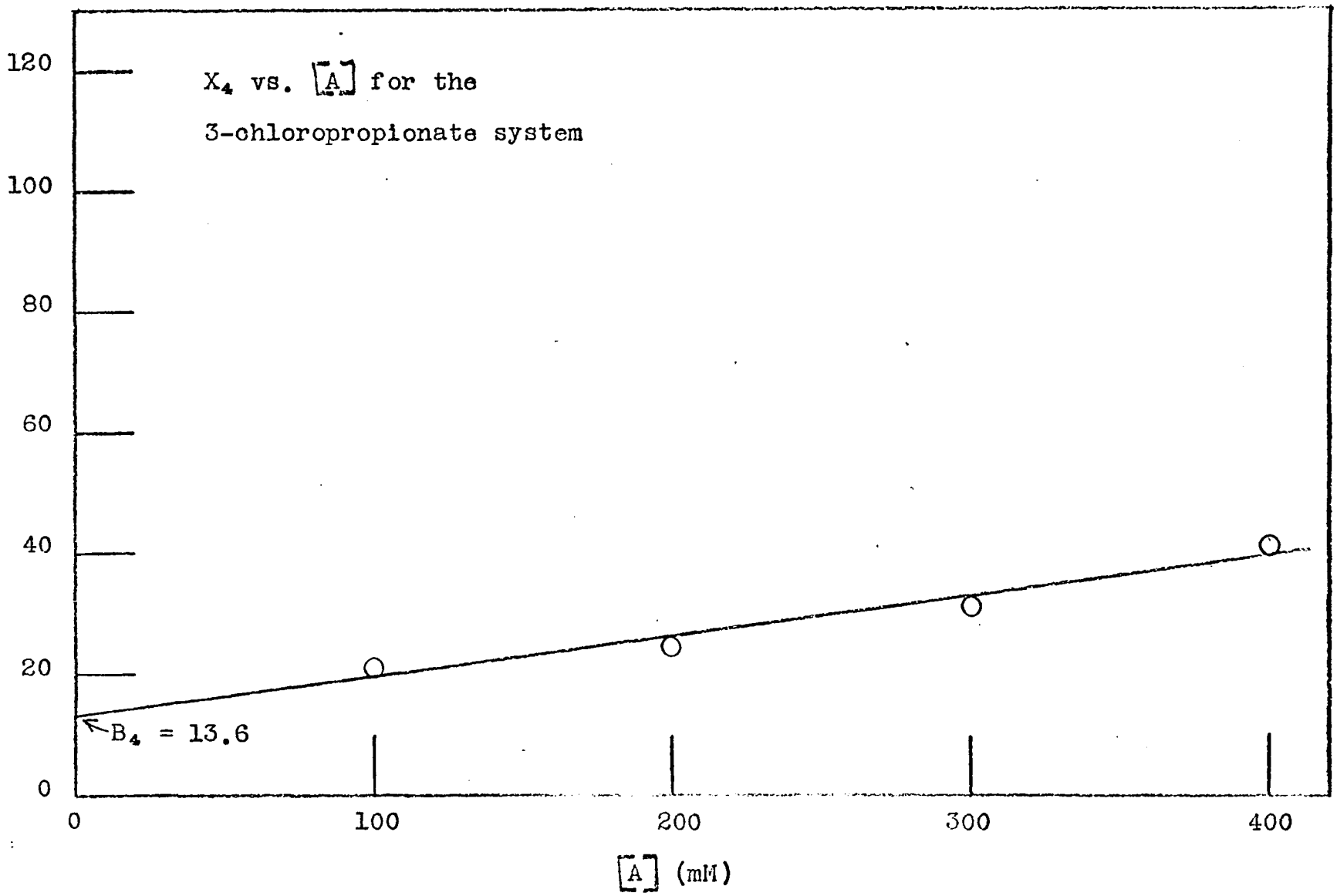
X_4 vs. [A] for the
3-chloropropionate system
120
100
80
60
40
20
0
X_4 ($\times 10^{-7}$) (M^{-4})
B_4 = 13.6
0
100
200
300
400
[A] (mM)

Fig. 19

TABLE IX

DISTRIBUTION OF THE METAL ION IN THE VARIOUS COMPLEXES AS A FUNCTION OF THE FREE LIGAND CONCENTRATION FOR THE 3-CHLOROPROPIONATE SYSTEM, I

Free Ligand Conc., [A]	$f_o = \frac{[M]}{C_M}(100)$	$f_1 = \frac{[MA]}{C_M}(100)$	$f_2 = \frac{[MA_2]}{C_M}(100)$	$f_3 = \frac{[MA_3]}{C_M}(100)$	$f_4 = \frac{[MA_4]}{C_M}(100)$	$f_5 = \frac{[MA_5]}{C_M}(100)$
mM	%	%	%	%	%	%
1.0	22.4	65.0	12.3	0.4	0.0	0.0
5.0	3.2	46.2	43.8	6.4	0.3	0.0
10.0	0.9	26.6	50.4	14.7	1.2	0.1
20.0	0.2	12.9	48.8	28.4	4.8	0.5
100	0.0	0.7	12.8	37.2	31.6	15.7
200	0.0	0.1	4.0	23.5	40.0	39.8
400	0.0	0.0	0.8	8.8	29.8	59.2

2-chloropropionate system, that there may be a tendency toward a maximum coordination number of six. Figure 20, which is a plot of $\bar{n}$ vs. [A] for all three systems, seems to reinforce this suggestion of a tendency toward hexa-coordination in the 2- and 3-chloropropionate systems.

In a previous report of a study of this type conducted by Sunden[1], six stability constants were reported on the basis of a maximum value of five for the ligand number. Six β_n values can be calculated and reported from the present data as well, and $\bar{n}$ reaches a value of 4.96 at [A] = 400 mM. Such a calculation required redefinition of the X_n values such that:

$$X_1 = \frac{(X - 1)}{[A]} = \beta_1 + \beta_2[A] + \beta_3[A]^2 + \beta_4[A]^3 + \beta_5[A]^4 + \beta_6[A]^5$$

$$X_2 = \frac{(X_1 - \beta_1)}{[A]} = \beta_2 + \beta_3[A] + \beta_4[A]^2 + \beta_5[A]^3 + \beta_6[A]^4$$

$$X_3 = \frac{(X_2 - \beta_2)}{[A]} = \beta_3 + \beta_4[A] + \beta_5[A]^2 + \beta_6[A]^3$$

$$X_4 = \frac{(X_3 - \beta_3)}{[A]} = \beta_4 + \beta_5[A] + \beta_6[A]^2$$

$$X_5 = \frac{(X_4 - \beta_4)}{[A]} = \beta_5 + \beta_6[A] \ .$$

Then the procedure for the calculation of β_n' reverted to that used previously, with β_6' representing the slope of the line obtained in an X_5 vs. [A] plot. As a result of the graphical procedures used to obtain the β_n values there was no change in the values β_1 through β_3 from those previously obtained. β_4 changed somewhat as it was now determined by the extrapolation of a smooth curve through the points previously plotted. This new plot is shown as Figure 21. β_5' and β_6' were obtained as the intercept and slope, respectively, of the plot of X_5 vs. [A] shown as Figure 22. The alternate set

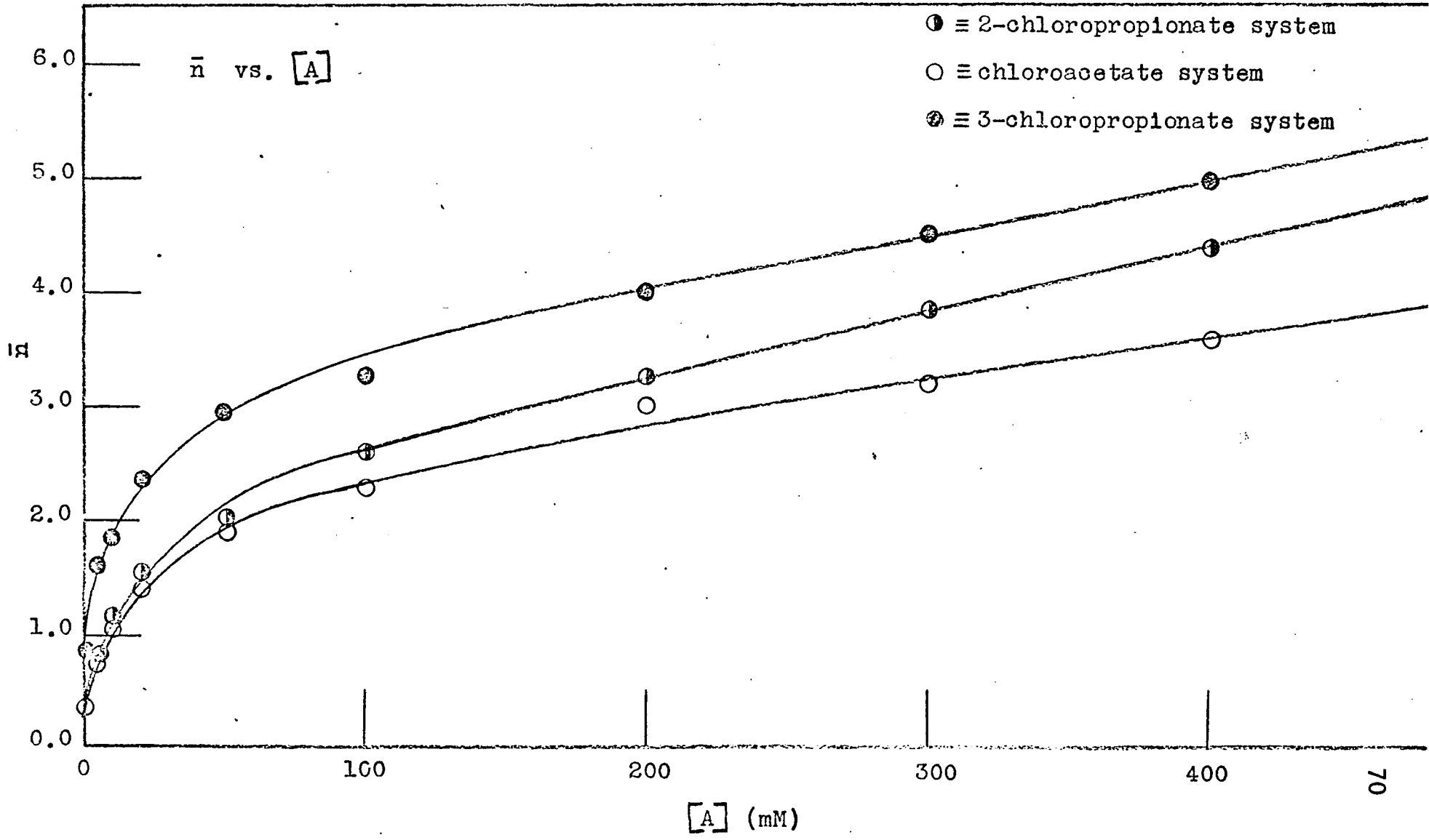
n̄ vs. [A]
◑ ≡ 2-chloropropionate system
○ ≡ chloroacetate system
◍ ≡ 3-chloropropionate system
6.0
5.0
4.0
3.0
2.0
1.0
0.0
n̄
0
100
200
300
400
70
[A] (mM)

Fig. 20

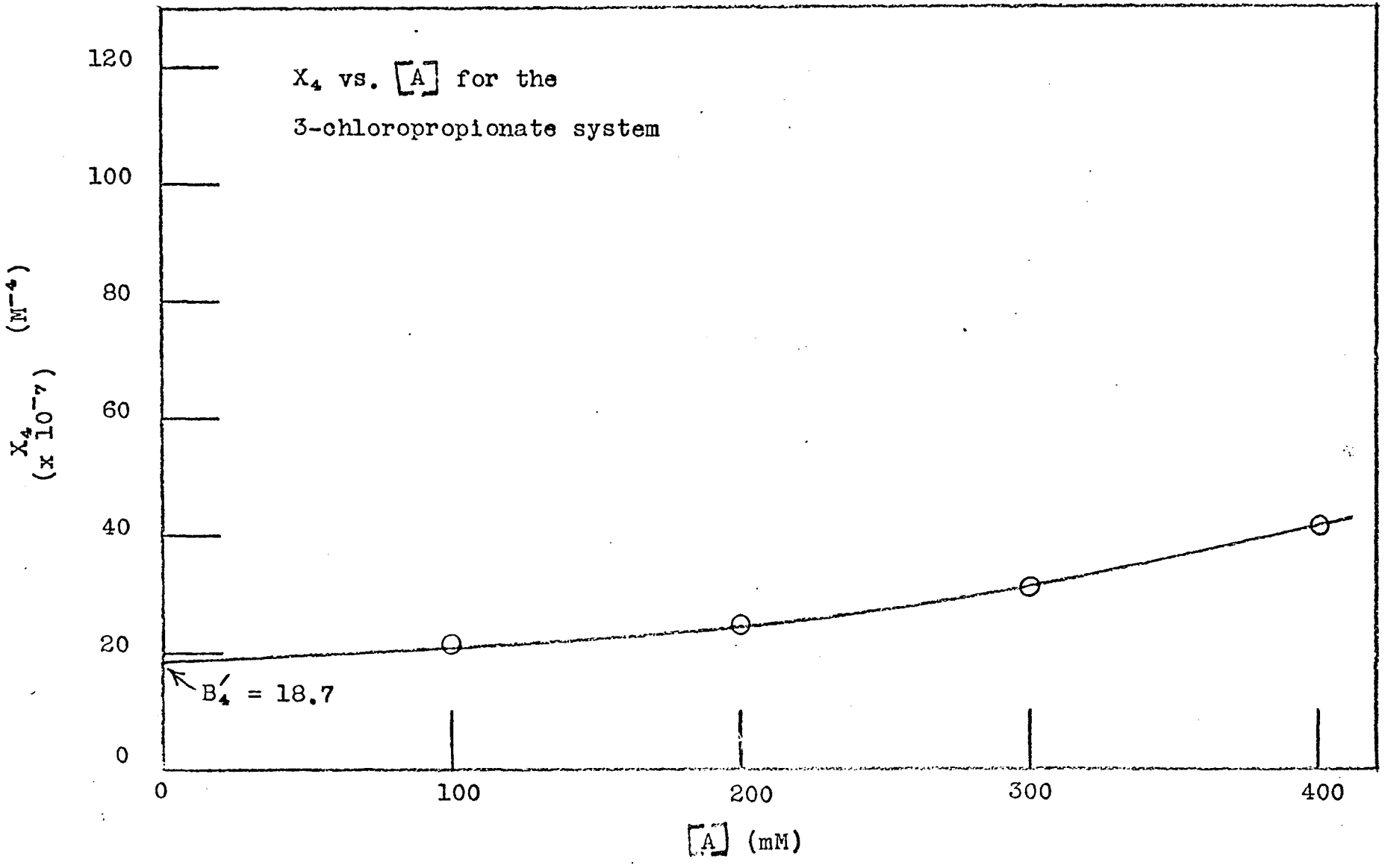
X_4 vs. [A] for the
3-chloropropionate system
120
100
80
60
40
20
0
X_4 ($\times 10^{-7}$) (M^{-4})
$B_4' = 18.7$
0
100
200
300
400
[A] (mM)

Fig. 21

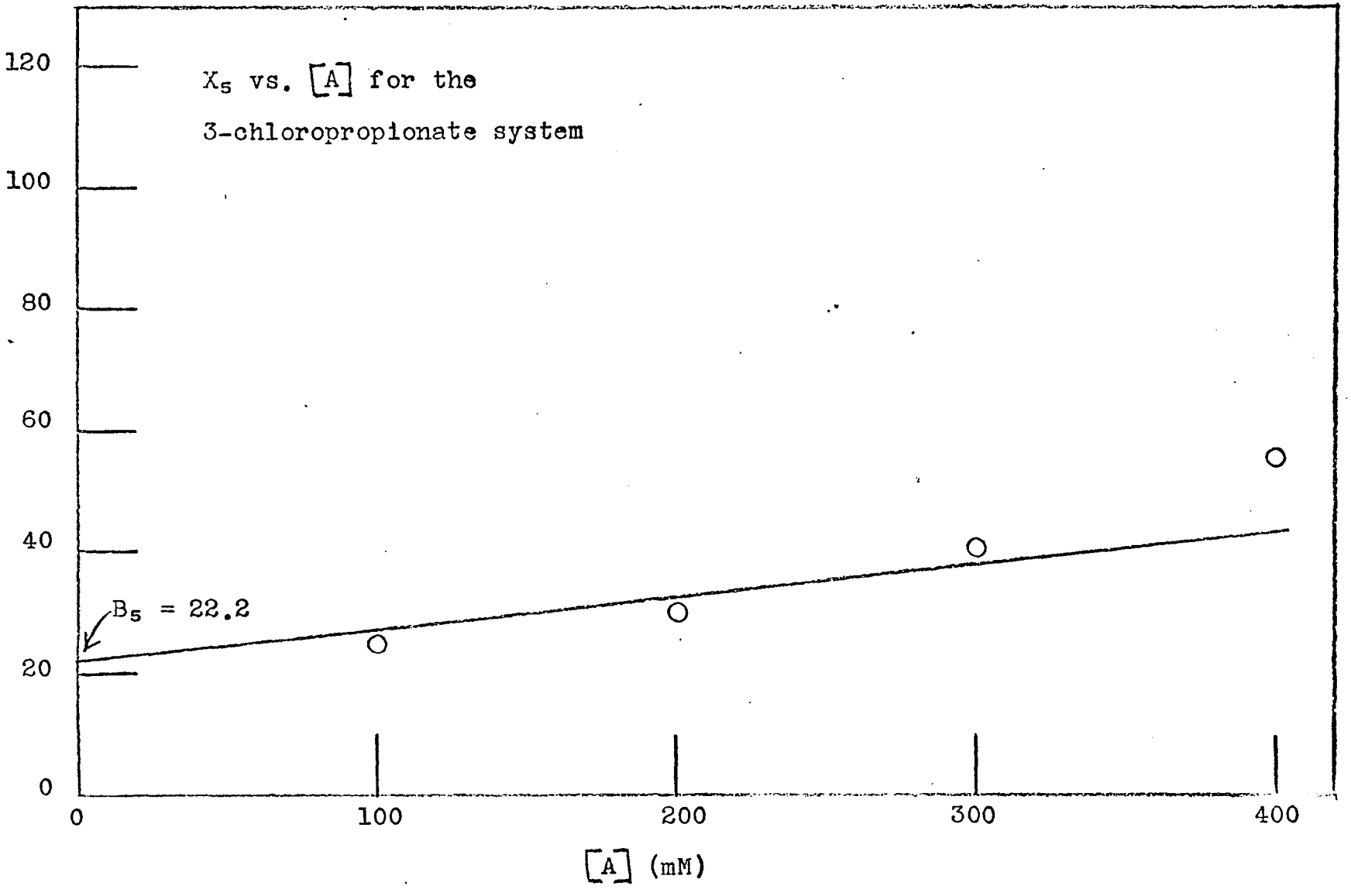
X_5 vs. [A] for the
3-chloropropionate system
120
100
80
60
40
20
0
X_5 ($\times 10^{-7}$) (M^{-5})
B_5 = 22.2
0
100
200
300
400
[A] (mM)

Fig. 22

of β_n' values was as follows:

$$\beta_1' = 2.9 \pm 0.4 \times 10^3 \ M^{-1}$$

$$\beta_2' = 5.5 \pm 0.9 \times 10^5 \ M^{-2}$$

$$\beta_3' = 1.6 \pm 0.4 \times 10^7 \ M^{-3}$$

$$\beta_4' = 1.9 \pm 0.8 \times 10^8 \ M^{-4}$$

$$\beta_5' = 2.2 \pm 1.2 \times 10^8 \ M^{-5}$$

$$\beta_6' = 1.0 \pm 0.7 \times 10^9 \ M^{-6}$$

This resulted in the following stepwise constants:

$$K_1' = 2.9 \times 10^3$$

$$K_2' = 190$$

$$K_3' = 29$$

$$K_4' = 11$$

$$K_5' = 1.2$$

$$K_6' = 4.5$$

The alternate set of β_n' values also resulted in a new calculated distribution of metal ion throughout the various complexes which is shown as Table X.

It seems reasonable at this point to attempt some type of assessment of the comparative dependability of the two sets of numbers. Both from an experimental and interpretative viewpoint, the extraction of six values from this data is probably not extremely meaningful. The maximum value of

TABLE X

DISTRIBUTION OF THE METAL ION IN THE VARIOUS COMPLEXES AS A FUNCTION OF THE FREE LIGAND CONCENTRATION FOR THE 3-CHLOROPROPIONATE SYSTEM, II

[A] (mM)	f_o (%)	f_1 (%)	f_2 (%)	f_3 (%)	f_4 (%)	f_5 (%)	f_6 (%)
1.0	22.4	65.0	12.3	0.4	0.0	0.0	0.0
5.0	3.2	46.2	43.8	6.4	0.4	0.0	0.0
10.0	0.9	26.6	50.4	14.7	1.7	0.0	0.0
20.0	0.2	12.9	48.8	28.4	6.7	0.2	0.0
100	0.0	0.7	12.8	37.2	44.1	5.1	2.3
200	0.0	0.1	4.0	23.5	55.8	12.9	11.8
400	0.0	0.0	0.8	8.8	41.5	19.2	35.0

$\bar{n} = 5$ would seem to indicate that the experimental tools are adequate to produce only five numbers. Furthermore, certain graphical approximations which may not be justified are required to obtain reasonable values of β_5' and β_6'. In general, it would appear that the β_n values are somewhat more dependable than the β_n' quantities, with the usual qualification that the final two numbers, β_4 and β_5, might best be interpreted as order of magnitude measurements. The one possible exception to this generalization is the β_4 quantity. As a result of the graphical interpretative techniques used, β_4' may well be a better value than β_4.

Observations

The primary objective of this work was to obtain the stability constants for indium(III) ion complexes with chloro-substituted carboxylic acid anions. The ligands used were chloroacetate, 2- and 3-chloropropionate ions. These stability constants are summarized in Tables XI and XII. Table XI lists the overall stability constants for the stepwise formation of the complexes (β_n values). Table XII shows the stepwise stability constants (K_n values).

A secondary aim of this study was to investigate the possible existence of any correlations between the stability constants and the acid dissociation constants. The stability constants determined by Sunden[1], under very similar conditions, are included in an attempt to make this investigation somewhat more meaningful. The acid dissociation constants of the pertinent carboxylic and substituted carboxylic acids are listed in Table XIII. The stability constants for the indium(III) ion complexes with these acid anions are given in Table XIV. The

TABLE XI

OVERALL STABILITY CONSTANTS OF INDIUM(III) COMPLEXES (25°C)

Ligand Ion	β_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	β_4 (M^{-4})	β_5 (M^{-5})	β_6 (M^{-6})
chloroacetate	4.8×10^2	1.0×10^4	1.5×10^5	2.0×10^5		
2-chloropropionate	5.2×10^2	1.8×10^4	1.9×10^5	7.0×10^5	2.0×10^6	
3-chloropropionate	2.9×10^3	5.5×10^5	1.6×10^7	1.4×10^8	6.4×10^8	
(β_n' values)*	———	———	———	1.9×10^8	2.2×10^8	1.0×10^9

*β_n' values were discussed in the 3-chloropropionate results section.

TABLE XII

STEPWISE STABILITY CONSTANTS OF INDIUM(III) COMPLEXES (25°C)

Ligand Ion	K_1 (M^{-1})	K_2 (M^{-1})	K_3 (M^{-1})	K_4 (M^{-1})	K_5 (M^{-1})	K_6 (M^{-1})
chloroacetate	480	21	15	1.3		
2-chloropropionate	520	35	10	3.7	2.8	
3-chloropropionate	2900	190	29	8.7	4.6	
(K_n' values)*	____	____	___	11	1.2	4.5

*K_n' values are identified in the 3-chloropropionate results section.

TABLE XIII

ACID DISSOCIATION CONSTANTS* OF THE VARIOUS ORGANIC ACIDS

Acid	K_a	t (°C)
Acetic	1.75×10^{-5}	20
Chloroacetic	1.38×10^{-3}	25
Propionic	1.34×10^{-5}	20
2-Chloropropionic	1.32×10^{-3}	18
3-Chloropropionic	1.01×10^{-4}	25
Formic	1.78×10^{-4}	20
Glycolic	1.48×10^{-4}	25
	1.46×10^{-4}	18

*All constants in this table were taken from ref. 37.

TABLE XIV

OVERALL STABILITY CONSTANTS OF THE VARIOUS INDIUM(III) COMPLEXES

Acetate Ligand (20°C)*

$\beta_1 = 3200$

$\beta_2 = 9 \times 10^5$

$\beta_3 = 8 \times 10^7$

$\beta_4 = 1.2 \times 10^9$

$\beta_5 = 1.7 \times 10^9$

$\beta_6 = 2 \times 10^{10}$

Chloroacetate Ligand (25°C)

$\beta_1 = 480$

$\beta_2 = 1.0 \times 10^4$

$\beta_3 = 1.5 \times 10^5$

$\beta_4 = 2.0 \times 10^5$

Propionate Ligand (20°C)*

$\beta_1 = 3700$

$\beta_2 = 2.3 \times 10^6$

$\beta_3 = 1.4 \times 10^8$

$\beta_4 = 1.2 \times 10^9$

$\beta_5 = 1.3 \times 10^{10}$

2-Chloropropionate Ligand (25°C)

$\beta_1 = 520$

$\beta_2 = 1.8 \times 10^4$

$\beta_3 = 1.9 \times 10^5$

$\beta_4 = 7.0 \times 10^5$

$\beta_5 = 2.0 \times 10^6$

continued-

TABLE XIV-2

Glycolate Ligand (20°C)*	3-Chloropropionate Ligand (25°C)
$\beta_1 = 850$	$\beta_1 = 2900$
$\beta_2 = 3.3 \times 10^5$	$\beta_2 = 5.5 \times 10^5$
$\beta_3 = 1.6 \times 10^7$	$\beta_3 = 1.6 \times 10^7$
$\beta_4 = 7.5 \times 10^7$	$\beta_4 = 1.4 \times 10^8$
$\beta_5 = 4 \times 10^8$	$\beta_5 = 6.4 \times 10^8$

Formate Ligand (20°C)*

$\beta_1 = 550$

$\beta_2 = 5.2 \times 10^4$

$\beta_3 = 5.0 \times 10^5$

$\beta_4 = 5 \times 10^6$

*All of the starred sets of stability constants were taken from ref. 1.

values shown in Table XIV are not all strictly comparable, as some were reported at 20°C and others at 25°C. It is very doubtful, however, if this temperature difference would exert any perceptible effect on the conclusions reached here (see Appendix II). There may be some question as to the validity of comparisons of quantities in Table XIII with those in Table XIV. All stability constants listed in Table XIV were determined at a total ionic strength of 2 M. The acid dissociation constants of Table XIII are the result of extrapolations to zero ionic strength. The quantities shown in Table XIII were taken from Kortum, Vogel and Andrussow.[37] Examination of the original literature [38-40], dealing with the determination of the dissociation constants of formic, propionic, glycolic and chloroacetic acids suggested that the tabulated acid constants may be meaningfully related to the stability constants in Table XIII. The acid constants at an ionic strength of about two differed from the same acid constants at zero ionic strength by much less than an order of magnitude.

Sunden[1] has noted in his paper a correlation between the increasing value of the stability constants and the decreasing value of the acid dissociation constants. An examination of the β_1 values for the systems he studied, acetate, propionate, formate and glycolate, seems to indicate roughly that a decrease in the acid constant by one order of magnitude results in the increase of β_1 by one order of magnitude. The relationship becomes more obscure if subsequent values of β_n are compared. A correlation of this type seems quite reasonable in the light of some more modern developments in acid-base theory. According to Pearson[41], the formation of the complex indium species would merely represent the substitution of the hard acid, indium(III) ion, for the proton,

which is the prototype of hard acids. Furthermore, a basic species which coordinates well with one hard acid should coordinate well with another hard acid. This line of reasoning seems to be particularly appropriate in the case of the formate, acetate, and propionate systems where it is difficult to envision any substantial chemical interactions occurring away from the carboxylate group of the ligand ion.

With the chlorosubstituted acids the induction effect, observable in the acid constants of these acids, is also detected in the stability constants reported. The chlorosubstituted ligand systems show an internal stability constant-acid dissociation constant correlation similar to that observed above; i.e., order of magnitude for order of magnitude. Here again, the relationship is pursued only through the β_1 values. The relationships between the substituted and unsubstituted acids, however, seem to be of a slightly different nature. Apparently, the stability constant increases by one order of magnitude as the acid dissociation constant decreases by two orders of magnitude. To clarify, consider the example of the acetate-chloroacetate systems: acetic acid is about two orders of magnitude weaker than chloroacetic acid, but the chloroacetate complex is only about one order of magnitude weaker than the acetate complex. This is not an exact relationship in all cases. Also, attention must be called again to the temperature and ionic medium disparities in these comparisons. Nevertheless, this interdependence, if real, may not be entirely untenable. In these chlorosubstituted ligand species, there would appear to exist the possibility of interactions with the indium ion in addition to those interactions that occur between the indium ion and the unsubstituted acid ligands. The limited number of constants presently available does not permit the formulation of any conclusions. It would be most interesting,

however, to examine the stepwise stability constants of indium(III) ion with the bromoacetate and iodoacetate systems when they have been determined.

SUMMARY

The overall stability constants and stepwise stability constants have been determined for indium(III) ion complexes with chloroacetate, 2-chloropropionate and 3-chloropropionate anions. The experimental work was done by means of a potentiometric titration procedure. All determinations were made at 25.00 $\pm$ 0.01°C and a constant total ionic strength of 2 M.

Chloroacetate ligand system. The overall stability constants for the indium(III)-chloroacetate complex system are as follows:

$\beta_1 = 4.8 \pm 0.4 \times 10^2\ M^{-1}$ $\beta_3 = 1.5 \pm 0.2 \times 10^5\ M^{-3}$

$\beta_2 = 1.0 \pm 0.1 \times 10^4\ M^{-2}$ $\beta_4 = 2.0 \pm 1.6 \times 10^5\ M^{-4}$

The stepwise stability constants for this system are:

$K_1 = 480\ M^{-1}$ $K_3 = 15\ M^{-1}$

$K_2 = 21\ M^{-1}$ $K_4 = 1.3\ M^{-1}$

2-Chloropropionate ligand system. The overall stability constants for the indium(III)-2-chloropropionate complex system are as follows:

$\beta_1 = 5.2 \pm 0.1 \times 10^2\ M^{-1}$ $\beta_4 = 7.0 \pm 1.5 \times 10^5\ M^{-4}$

$\beta_2 = 1.8 \pm 0.15 \times 10^4\ M^{-2}$ $\beta_5 = 2.0 \pm 1.1 \times 10^6\ M^{-5}$

$\beta_3 = 1.9 \pm 0.3 \times 10^5\ M^{-3}$

The stepwise stability constants for this system are:

$K_1 = 520\ M^{-1}$ $K_4 = 3.7\ M^{-1}$

$K_2 = 35\ M^{-1}$ $K_5 = 2.8\ M^{-1}$

$K_3 = 10\ M^{-1}$

3-Chloropropionate system. Two sets of stability constants were determined for this system.

The first set, derived on the basis of a maximum experimental coordination number of five, are:

overall stability constants

$\beta_1 = 2.9 \pm 0.4 \times 10^3\ M^{-1}$ $\beta_4 = 1.4 \pm 0.6 \times 10^8\ M^{-4}$

$\beta_2 = 5.5 \pm 0.9 \times 10^5\ M^{-2}$ $\beta_5 = 6.4 \pm 4.5 \times 10^8\ M^{-5}$

$\beta_3 = 1.6 \pm 0.4 \times 10^7\ M^{-3}$

stepwise stability constants

$K_1 = 2900\ M^{-1}$ $K_4 = 8.7\ M^{-1}$

$K_2 = 190\ M^{-1}$ $K_5 = 4.6\ M^{-1}$

$K_3 = 29\ M^{-1}$

The second set of constants for this system, derived on the basis of a maximum coordination number of six, are:

overall stability constants

$\beta_1' = 2.9 \pm 0.4 \times 10^3\ M^{-1}$ $\beta_4' = 1.9 \pm 0.8 \times 10^8\ M^{-4}$

$\beta_2' = 5.5 \pm 0.9 \times 10^5\ M^{-2}$ $\beta_5' = 2.2 \pm 1.2 \times 10^8\ M^{-5}$

$\beta_3' = 1.6 \pm 0.4 \times 10^7\ M^{-3}$ $\beta_6' = 1.0 \pm 0.7 \times 10^9\ M^{-6}$

stepwise stability constants

$K_1' = 2900\ M^{-1}$ $K_4' = 11\ M^{-1}$

$K_2' = 190\ M^{-1}$ $K_5' = 1.2\ M^{-1}$

$K_3' = 29\ M^{-1}$ $K_6' = 4.5\ M^{-1}$

The relative validity of these two sets of values is discussed.

The distribution of the metal ion in various complexes as a function of free ligand ion concentration was calculated and tabulated for each system.

Finally, certain observations were made regarding the relationships existing between the stability constants of the indium ion-weak acid anion complexes and the acid dissociation constants of these same weak acids.

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APPENDIX I

Metal Ion Hydrolysis

In an attempt to gain some insight into the experimental behavior to be expected in the presence of extensive hydrolysis of the chloro-substituted acids used in this study, an additional operation was undertaken. A complete set of determinations were made using 4:1 and 1:1 chloroacetate buffer solution in which the hydrolysis of chloroacetic acid had progressed to a considerable degree. This solution then contained significant quantities of hydroxyacetic acid and chloride ion. The actual results of this study are not reported in this paper as they have little value with respect to the determination of stability constants. The results are of great interest, for comparative purposes, because they disclose some very curious trends in the measured e.m.f.'s. The range of E_o values in the hydrolyzed ligand solutions was about three times that in the "unhydrolyzed" solutions reported in the body of the thesis. The E values for the metal ion solution with initial $In(ClO_4)_3$ concentration of 10 mM showed a trend in the hydrolyzed system which was exactly opposite the trend in the chloroacetate system reported in this paper. The E values in the hydrolyzed solutions decreased throughout the titration and covered about a 30 to 40% smaller range than the reported values. The E values obtained for the solutions in which the initial concentration of indium(III) ion was 20 mM showed a minimum fairly early in the titration and then increased throughout the remainder of the determination in the case of the hydrolyzed system. The e.m.f. range in the hydrolyzed solutions

was only about 20% of the e.m.f. range in unhydrolyzed solutions. The E values for the hydrolyzed solutions in which the initial $In(ClO_4)_3$ concentration was 40 mM also exhibited an early minimum followed by an increase throughout the remainder of the titration. The e.m.f. range covered in the hydrolyzed system was only about two-thirds that in the unhydrolyzed system.

No attempt is made here to interpret the results of the spurious chloroacetate ligand system. Rather, it is hoped that some, at least tentative experimental, ground-rules have been established for the detection of extensive acid hydrolysis effects in systems of this type. If these trends do, in fact, serve as some sort of guidelines, it would appear that the effects of extensive ligand acid hydrolysis have been avoided in this study.

APPENDIX II

Temperature Dependence of Stability Constants

In work carried out as a preliminary to the present study, the stability constants (β_n values) for the acetate complexes of indium(III) ion at 25°C were obtained. Although this work was admittedly of a crude nature and was designed primarily to examine the apparatus and techniques used in the present study, the results of this preliminary study are of some aid in estimating the magnitude of the temperature effect. It was found that for those constants which could be accepted as being reasonably dependable, the 5° temperature differential in the acetate system resulted in somewhat less than an order of magnitude effect. As the conclusions drawn in the observations section of this paper, regarding acid constant-stability constant correlations, are based fundamentally on order of magnitude relationships, the temperature differential should be of little moment.